Research Paper

Hydrogeochemical Study of Morang River Draining Rajmahal Basalt: Implication to Mineral Equilibria and Chemical Weathering

PREM CHAND KISKU, HALDHAR KUMAR and JITENDRA KUMAR PATTANAIK*

Department of Geology, Central University of Punjab, Bathinda 151 001, India

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In this study geochemical investigation of Morang river, draining Rajmahal basalt was carried out to understand the basalt weathering and neoformations. This seasonal river was sampled during post-monsoon period along with groundwater samples. Concentration of Ca^{2+} and Mg^{2+} is high in the upper reach of Morang River and lower reach is relatively high with $\text{Na}^+ + \text{K}^+$ cations. In all the samples, HCO_3^- is a dominant ion. River and groundwater samples shows Ca^{2+} - Mg^{2+} - HCO_3^- hydrochemical facies. Dissolution of primary minerals and secondary minerals present in the voids of basalt are the major ion source to the river. Unusual high NO_3^- at few locations indicates the anthropogenic input. The $p\text{CO}_2$ is out of equilibrium with atmosphere ($>10^{-3.5}$) in water samples, indicating possible contribution from the soil CO_2 . All the water samples are either under-saturated or near saturation with respect to carbonates, except two river water. Mineral stability diagram suggests that water is in equilibrium with kaolinite, indicate the limited chemical weathering process in source area. Elemental ratio and Principle Component Analysis (PCA) suggests preferential weathering of pyroxene compared to plagioclase minerals; and pH controlled ionic concentration in the river and groundwater.

Keywords: Chemical Weathering; Saturation Index; Principle Component Analysis (PCA); Mineral-Water Equilibria

Introduction

Geochemical characteristics of natural water reveal different information related to processes occurred on the earth surface (Olive *et al.*, 2003; Zhao and Zheng, 2015). Ionic composition of water and presence of clay minerals in the same environment are related and controlled by the type of rock-water interaction and the intensity of chemical weathering (Taylor and McLennan, 1985; Elango and Kannan, 2007; Anderson *et al.*, 2007; Depetris, 2014). The atmospheric CO_2 dissolved in rainwater to form weak carbonic acid and reacts with primary minerals (Bluth and Kump, 1994; Mathé *et al.*, 1999; Kump *et al.*, 2000). Congruent or incongruent weathering of primary mineral releases ions, solutes and/or nutrients into the river and groundwater. Anthropogenic input is also contributed towards ionic charge of river water and it can mislead the estimation of associated mineral stability (Berner and Berner 1987; Sarin *et al.*, 1989;

Singh and Hasnain 2002). The ions and solute abundances in river water are directly related to mineralogy of host rock and their nature of solubility (Sarin *et al.*, 1989). Moreover, geochemical composition of river water also aids to theoretical prediction of existing equilibrium condition with primary and secondary mineral phases, depending on the environmental condition (Elango and Kannan, 2007). Stability fields depicts environment necessary for mineral to be concurred at equilibrium and to determine which minerals are stable or unstable at certain geochemical environment (Garrels and Christ, 1965; Helgeson *et al.*, 1969). Most of the river drains diverse lithology with varying proportion of primary minerals, hence establishing ionic contribution from different lithology and mineral equilibrium is complex. Where, selection of *a priori* is a challenge. Therefore, it is important to study the river draining monolithological terrain and to establish their hydrochemical characteristics.

*Author for Correspondence: E-mail: jitendra.bapi@gmail.com

Basalts are highly susceptible to chemical weathering due to its fine grain nature and presence of Ca-Na, Fe-Mg bearing minerals (Mathé *et al.*, 1999; Dupré *et al.*, 2003; Vigier *et al.*, 2006). River draining basaltic terrain generally carries significant amount of dissolved load where bicarbonate is a major ion. Major anions like HCO_3^- and SO_4^{2-} in water is mainly produced due to atmospheric CO_2 dissolution and oxidation of sulfide minerals respectively (Singh *et al.*, 2008). Mineralogical composition of the Rajmahal basalt is plagioclase, pyroxene, opaque iron bearing minerals and glass. However, top part of the basaltic flow is rich in voids and vesicles filled with various secondary minerals like palagonite and chlorophaeite (Sarbadhikari, 1966). Some of these secondary minerals are assumed to be derived from the alteration of pyroxene, iron-bearing minerals and primary glasses, which are chiefly belongs to smectite and vermiculite in Rajmahal (Sarbadhikari, 1966). During basalt weathering, primary minerals transformed to clay by ion exchange and/or neoformation reaction (Eberl *et al.*, 1984), and rate of these reactions are linked with climate and influenced by the concentration of atmospheric CO_2 (Berner *et al.*, 1983; White and Blum, 1995; White *et al.*, 1999; Kump *et al.*, 2000; Drever, 2005; Green *et al.*, 2006; Kent and Muttoni, 2013; Li and Long, 2014). The Deccan basalt was studied for extensively understanding such geological processes (Salil *et al.*, 1997; Deshmukh *et al.*, 2012). Geochemical modelling also supported the widespread dissemination of secondary minerals like smectite and kaolin group (Mitra *et al.*, 2017) in the Deccan Trap region.

In this study, water samples from Morang river draining exclusively Rajmahal Basalt, Jharkhand; few samples from Gumani river draining Basalt, Chhotanagpur Gneiss and Gondwana supergroup; and groundwater were collected (Table 1). The small catchment area of Morang provides an opportunity to study a monolithological terrain to understand the basalt weathering and neoformations. Samples were also analyzed to understand the equilibrium between mineral phases and natural water in the catchment area. This will help to understand the controlling geochemical parameters, for various surficial processes. In addition to this geochemistry of river water draining Deccan Volcanic Provinces (DVP) (Dessert *et al.*, 2001) is compared to check the mineralogical control in the surficial processes. The

DVP and Rajmahal basalts are lying almost in similar latitudinal range. However, the geological ages of the two basaltic terrains are different. In this study, contribution of rainwater in the river water chemistry and evapotranspiration loss was not considered, assuming that these factors are part of the process and the product what we see as river water. Primarily, the attempt is made to understand the chemical weathering, controlling factors and thermodynamic equilibrium of water and minerals in the Rajmahal basaltic terrain. Principal Component Analysis (PCA) is used to differentiate source of ions, to establish link between controlling parameter and geochemical processes (Jeen *et al.*, 2001; Singh and Hasnain, 2002; Jeevanandam *et al.*, 2007; Krishna *et al.*, 2009; Ranjan *et al.*, 2013, Kumar *et al.*, 2015; Ravikumar and Somashekar, 2017) associated in Rajmahal drainages.

Study Area

The catchment area of river Morang of Jharkhand, lies on Rajmahal basalt and situated between ranges of latitude $24^{\circ}50' 52.08''$ N - $25^{\circ}10' 59.8''$ N, and longitude $87^{\circ}33' 16.16''$ E - $87^{\circ}42' 36.8''$ E. Along the course of the river recent alluviums are overlying the basalt. In the catchment area, soil is fertile and black in color. Rajmahal basalt is weathered to laterite and lateritic caps are found at many places. The river Morang originates near Durga Tola village in the north and confluence with Gumani river near Barhait towards south. General trend of the river is north-south. Gumani river originates from Chotanagpur Gneiss and it drains small patch of Gondwana supergroup rock followed by the Rajmahal basalt before draining in to river Ganga near Farakka barrage, West Bengal. Rajmahal Basalt shows varying thickness and consists of multiple basalt flow indicating several phase of volcanic eruptions (Klootwijk, 1971). Total 28 flows having 331m thickness is reported by Geological Survey of India, from the borehole data. However only 15 flows are demarcated in the outcrop (Mahadeven, 2002). Based on the present day topography and nature of basalt flow, researchers were identified multiple eruption centers around the study area. Maximum thickness of the Rajmahal flow is observed nearly to be 600m (Klootwijk, 1971). The Rajmahal basalt was derived from the Kerguelen hotspot during Early Cretaceous age and the $^{40}\text{Ar}/^{39}\text{Ar}$ systematic dating shows the age of eruption

Table 1: Physical and chemical parameter of water samples. River and bore well water sample location of Morang and Gumani River. Locations are arranged from upstream to downstream direction, however, tributaries are arranged depending up on the position of their confluence with main river. *Distance (km) measured of sample location from confluence of Gumani and Ganga River. Bdl: below detection limit, na – not available

Name	Latit- tude (N)	Longi- tude (E)	Place Name	Distance (km)*	pH	Temp. (°C)	Cond ($\mu\text{S cm}^{-1}$)	TDS (ppm)	Salinity (ppm)	Cations ($\mu\text{mole/l}$)					Anions ($\mu\text{mole/l}$)				Trace ($\mu\text{mole/l}$)				
										Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	F ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Si	Sr	Ba	Fe	
Morang River	RW1	25° 10' 59.8"	87° 40' 1.3"	Durgatola	103	8.13	25.7	179.3	127	88	237	282	259	26.5	1919	7.1	50.0	7.2	12.7	106	1.23	0.10	3.2
	RW10	25° 07.329'	87° 39.198'	Bhurkunda	95	8.15	26.1	181.3	129	89	252	304	275	33	2279	8.0	65.9	8.9	4.5	71	1.19	0.16	3.0
	RW2	25° 07' 07"	87° 38' 51.2"	Sabaiya	94	8.01	26.4	187.8	133	92	222	299	258	13	2399	7.3	54.5	8.3	4.0	86	1.29	0.16	3.0
	RW13	25° 06' 52.99"	87° 38' 22.48"	Sabaiya	92	7.87	24.8	120.1	86	61	109	204	183	45	1560	7.0	48.5	12.2	5.0	50	0.78	0.13	1.7
	RW4	25° 06.508'	87° 37.974'	Turua	90	8.10	27.6	191.5	136	94	244	305	269	14	2459	6.8	49.8	7.4	5.9	97	1.34	0.16	3.2
	RW9	25° 04' 59.6"	87° 37' 38.4"	Majhauna	85	8.15	26.6	186.0	132	91	191	296	263	24	2519	7.6	56.8	12.3	4.8	110	1.19	0.16	2.8
	RW7	25° 03.483'	87° 36.87'	Simra	80	8.02	26.9	172.5	122	85	196	272	247	24	1800	8.9	62.0	11.7	6.3	54	1.21	0.16	2.7
	RW6	25° 01.9858'	87° 36.124'	Chapgawan	78	8.02	27.4	190.3	135	93	235	294	289	27	2099	9.6	71.6	13.2	8.4	82	1.31	0.17	3.5
	RW18	24° 59' 42.14"	87° 36' 1.93"	Chasganwan	66	8.10	26.9	202.0	143	99	232	324	314	66	2279	9.6	83.4	23.3	4.8	na	1.23	0.21	3.2
	RW17	24° 57' 24.64"	87° 35' 46.82	Phulbhanga	60	8.02	26.1	177.4	126	87	185	274	299	48	2279	8.4	75.7	14.6	4.0	122	1.25	0.19	2.6
Tributaries (Morang R.)	RW22	24° 54' 11"	87° 36' 32.7"	Paharpur	50	7.88	27.7	189.0	134	93	191	296	374	74	2459	8.5	90.0	17.8	5.5	103	0.99	0.24	3.0
	RW5	25° 07.8223'	87° 37.862'	Kordhia	88.6	8.13	27.3	185.5	131	91	244	288	252	21	2039	6.5	46.1	6.7	5.6	96	1.30	0.14	3.0
	RW3	25° 05.701'	87° 37.911'	Dighi	88.2	8.01	28.0	225.0	160	110	302	395	403	28	2639	11.7	30.2	7.6	1.7	74	1.40	0.21	3.6
	RW12	25° 05' 43.2"	87° 37' 08.30"	Matia	88	7.96	25.1	198.5	141	97	269	323	266	50	2099	8.0	52.8	19.0	5.8	101	1.17	0.15	3.4
	RW8	25° 03.787'	87° 37.312'	Gorda	81	8.03	27.6	283.0	201	137	387	471	416	29	3359	9.9	79.7	12.8	4.7	78	1.31	0.40	4.8
	RW11	25° 03' 31.25"	87° 35' 49.98"	Chhotakusma	78.5	8.08	24.8	188.8	139	92	228	289	292	52	2159	9.5	56.5	14.3	3.9	83	1.21	0.17	3.0
	RW20	25° 01' 0.3"	87° 36' 59"	Bansjori	71	8.06	27.1	162.6	115	81	137	266	233	29	2099	5.6	37.5	15.0	4.5	118	1.16	0.15	2.4
	RW21	25° 01' 21.3"	87° 35' 21.4"	Kalkha	73	8.34	27.8	282.0	201	137	373	442	580	52	3659	14.6	105.5	12.9	bdl	62	1.49	0.28	4.7
Gumani R.	RW19	24° 59' 59.6"	87° 34' 23.36"	Rampur	75	8.26	26.2	249.0	177	121	294	415	486	29	2459	10.8	75.1	18.8	2.3	42	1.40	0.17	3.8
	RW15	24° 53' 26.83"	87° 35' 25"	Singa	54	8.30	26.8	180.5	128	89	170	280	286	31	2159	7.9	57.8	17.3	4.6	75	1.22	0.16	2.6
	RW14	24° 50' 52.08"	87° 42' 36.8"	mjhohor	32	8.15	25.9	180.0	128	89	176	270	274	27	2219	8.5	69.8	15.4	5.4	60	1.27	0.18	2.6
Groundwater	RW16	24° 53' 37.67"	87° 33' 16.16"	Simaldhab	60	8.36	26.7	296.0	211	144	421	481	483	43	3419	11.7	73.0	15.5	1.1	80	1.42	0.23	4.8
	GW1	25° 07.881'	87° 37.569'	Kordhia		6.55	27.9	504.0	359	245	677	723	1007	21	2999	4.5	576.5	68.2	1077.4	204	1.74	0.02	14.3
	GW2	25° 03.257'	87° 36.944'	Simra		6.69	26.7	615.0	435	299	1045	921	1302	33	5039	10.8	840.4	175.0	54.0	178	3.09	0.24	9.8
	GW3	25° 04' 58.28"	87° 36' 27.37"	Majhauna		6.94	28.0	420.0	298	203	497	209	1389	23	3359	10.7	995.5	52.0	239.9	167	1.42	0.02	5.7
	GW4	24° 51' 19.98"	87° 41' 16.26"	Amjhohor		6.55	28.7	390.0	276	188	509	520	997	5	4319	7.8	73.8	33.4	2.0	303	1.15	0.01	5.4

Fig. 1: Map of the study area with sample location. Grey shade (dark) represents Rajmahal basalt outcrops and yellow color shows the recent alluvium. Gondwana supergroup rock and Chhotanagpur Gneiss is exposed in the western and southwest corner of the figure, respectively

is 117 ± 1 Ma (Mahoney *et al.*, 1983; Baksi, 1995; Kent *et al.*, 2002). This volcanic formation was exposed on the continental margin and area is cropping out over an area of nearly 4300 Km². The Rajmahal basalt primarily comprises of quartz-normative tholeiitic, minor olivine-basalts along-with basaltic andesite. The high-grade Precambrian rock of Chotanagpur gneissic and the sequence of Gondwana supergroup surrounding the Rajmahal basalt in the west, alluvial sediments of Ganga river system is in the North and East, rocks of Upper Gondwana Supergroup and Quaternary alluvium lies in the south of Rajmahal basalt (Ball, 1877; Sengupta, 1988; Storey *et al.*, 1992).

The study area receives S-W monsoonal rainfall during the month of June to September and average rainfall is nearly 1550 mm. It experiences humid to sub-humid tropical climate. The average maximum and minimum temperature throughout the year is 44.4°C and 6.8°C respectively (Bhattacharji, 2012;

GWIB, 2013; Ranjan and Parida, 2019). Gumani river and its tributaries are seasonal and maximum discharge may go up to 97.60 m³/sec (minimum discharge is recorded to 0.33 m³/sec) during monsoon period at Gumani barrage, where the cross sectional width of the river is 100 m (State Hydrology data 2018). Lean to no flow is observed during non-monsoon period. Gumani river basin shows dendritic drainage pattern, meandering in the middle and lower reaches (Fig. 1). The basement is mainly composed to basalt, except flank of Dubrajpur formation. Laterites are covered and are in-situ origin, mostly yellowish-red in color and other stratigraphic formations are alluviums. The advantageous properties of laterite, it acts as good reservoir to hold water due to its porous and permeable properties. The episodic flow of the lava formed the different litho-units, which are the main water bearing horizons in base rock formations. Massive bedrocks (basalt) are hard and compact in nature with negligible primary porosity and permeability, while active chemical

weathering creates secondary porosity as joints and fractures at sub surface horizons. These joints and fracture favorably acts to permeable of groundwater, their holding capacity and recharge to the aquifer. Water bearing zone occurs in depth range of 15-40m, interflows within the weathered zone. This zone is probably connected to the shallow aquifer in the form of joints and fractures and forms semi confined aquifer. Whereas depth below the 40m, due to compact nature and unavailability of significant fractures, it is completely cut-off to the lower aquifers.

Methodology

During post monsoon season (October 2017), the water samples were collected from bore well and river Morang and Gumani from different locations as indicated in the Fig. 1. Among 26 water samples, 22 numbers of samples were from river and four numbers of samples were collected from the bore well (Table 1). Sampling locations were selected to cover major tributaries of Morang and the confluence to check the contribution from each sub-catchment. Samples were collected from the middle of the river to avoid local inhomogeneity and contaminations, using Poly Propylene (PP) bucket and 500ml jar after copiously rinsing with ambient water. Groundwater samples GW1–GW3, were collected from the Morang catchment area, whereas, GW4 was collected near the Gumani river (RW 14).

Using EutechTM make (PCTestr35) multi-parameter pocket tester, samples were analyzed in the field for pH, Salinity, Temperature, TDS and Electrical Conductivity (EC). For alkalinity measurements, Hanna make HI3811 test kit was used. Further samples were filtered immediately using PP filtration unit, oil free vacuum pump and nylon membrane filter with pore size of 0.45 μm . Filtered samples were kept in two 125 mL in polypropylene bottles for anion and cation analysis. Aliquots used for cation analysis was acidified using ultrapure nitric acid and pH maintained at two. Measurements of anion such as F^- , Cl^- , SO_4^{2-} and NO_3^- were carried out using Dionex ICS 5000 plus (Thermo Scientific®) Ion Chromatography System. However, cations and selected trace elements were analyzed using quadrupole ICP-MS (Xseries, Thermo Scientific®). Internal standards and check standards at certain intervals were used during analysis to monitor

analytical precision and instrumental drift. Analytical uncertainties of the measurement for different ions vary from $\pm 2\%$ to $\pm 8\%$.

Results

River Water

River water samples were light yellowish to light brownish in color prior to the filtration due to the presence of suspended materials; however groundwater samples were colorless and free from the particulates. Physico-chemical parameters, major ion and trace element concentration is listed in the Table 1. River water samples were near alkaline, where highest pH (8.36) was recorded from a tributary of Gumani river (RW 16) near Simaldhab village. In Morang river, maximum pH value (8.34) was measured from its tributary (RW 21) near Kalkha village and lowest pH (7.96) was also observed in a tributary (RW12) at Matia village. Similar to pH, highest EC ($296 \mu\text{Scm}^{-1}$) was observed from RW16, whereas a tributary shows maximum EC value ($283 \mu\text{Scm}^{-1}$) in Morang catchment area. The lowest EC ($120 \mu\text{Scm}^{-1}$) was observed from the Morang river (RW13) near Sabaiya village. Maximum salinity of 144 ppm (NaCl equivalent) was recorded from RW16 and minimum salinity of 61 ppm (NaCl equivalent) observed from RW13. In the main stream of Morang river, sample collected from the RW13 shows minimum concentration for most of the major ions and trace element except for K^+ , F^- , SO_4^{2-} , NO_3^- and Ba. Higher concentrations of ions are observed towards the lower reach of Morang river. As the concentration of ions and water discharge from different tributaries of Morang are different, therefore the general trend of concentration along the river is difficult to establish. A tributary (RW5) is joining the Morang river between sample location RW13 and RW4, and concentration of most of the ions at RW4 are close to the RW5. If we consider binary mixing then contribution from RW5 is higher compared to RW13. Before the confluence of above tributary, channel width of the Morang river is narrow and channel width increases towards lower reach after the confluence. Among ions Ca^{2+} , Mg^{2+} , Na^+ and HCO_3^- are dominating in the Morang river water and its tributaries. Around 90-95% of the total anion is represented by the HCO_3^- in the river water. Charge balance of the river water samples is poor and it skewed towards the anion. Excess anion is due

to the presence of high bicarbonate concentration. Presence of soil CO_2 and other organic acid lead towards the charge imbalance in the surface water as reported for other rivers (Heikkinen, 1990; Viers *et al.*, 2000). Cation like Na^+ and K^+ is dominating towards lower reach whereas, Ca^{2+} and Mg^{2+} are in the upper reach of the Morang river. Among tributaries, sample RW20 shows lower concentration of ions, RW21 and RW8 shows higher concentration compared to others. Concentration of Sr and Ba does not show much variation in the river water. Highest concentration of NO_3^- is observed in the RW1 sample, which was collected from the upper reach and in the other part of the Morang river and its tributaries shows lower value. In case of Si concentration, RW17 shows the maximum concentration. Sample (RW16) collected from a tributary of Gumani river shows highest concentration of ions and trace element, except NO_3^- . This tributary join Gumani river upstream of RW15 sample location and Morang river confluence lies between RW15 and RW14. However, sample RW14 and 15 of Gumani river shows similar values, indicates Morang river contribution is not affecting much the ionic budget of Gumani river.

Groundwater

Compared to river water, groundwater is slightly acidic, the pH of groundwater samples ranged from 6.55-6.94. The EC of groundwater ranges from 390-615 $\mu\text{S}/\text{cm}^{-1}$ and TDS ranges from 276-435 ppm. Highest Ca^{2+} concentration (1045 $\mu\text{mole}/\text{l}$) was observed in the GW2 collected near to the RW7. Concentrations of Ca^{2+} in river water were much lower compared to the groundwater in that area. Similarly, concentration of other cations, bicarbonate, sulphate and Sr, are highest in GW2 sample. Unusual high concentration of NO_3^- was observed in the GW1 sample and to cross check the value, repeat measurements were carried out. Sample GW4 shows highest Si concentration and lowest NO_3^- , Cl^- and SO_4^{2-} concentration. Similar to river water, bicarbonate followed by Cl^- dominates the groundwater anionic budget. Compared to river water samples, concentrations of the major cations in groundwater samples are much higher.

Ionic Strength and Activity

Ionic strength ($I = \frac{1}{2} \sum m_i z_i^2$; where m_i -molar concentration of ions and z_i -charges, Garrels and

Christ, 1965; White, 2003) was calculated (Table 2) and the average value for river and groundwater samples are 2.6×10^{-3} and 3.5×10^{-3} respectively. The measured Electrical Conductivity (EC) and the calculated I for the river water is related as $I = 1.44 \times 10^{-5} \times \text{EC} \times (-0.0003)$ with $R^2 = 0.83$; whereas groundwater shows $I = 1.48 \times 10^{-5} \times \text{EC} \times (-0.0014)$ with $R^2 = 0.94$ (Fig. 2). The relation of EC and I is comparable with the reported value of $I = 1.6 \times 10^{-5} \times \text{EC}$ (Russell, 1976). The activity of ions for each samples were estimated as: "activity" $[a] = \gamma \times c$, where "c" is the concentrations in mole/l, and γ activity coefficient. As the ionic strength of the samples are less than 0.1 ($I < 0.1$), the activity coefficient was

calculated as $-\log \gamma = \frac{AZ^2\sqrt{I}}{1 + aB\sqrt{I}}$ (White, 2003), where,

the values of constant A, B and a was taken from Garrels and Christ, (1965). The sum of activity of cations (a^+) and anions (a^-) is observed to be positively correlated. However, the river water shows the correlation of $a^+ = (0.27 \times a^-) + (7 \times 10^{-5})$ with $R^2 = 0.7$, whereas groundwater represents $a^+ = (0.56 \times a^-) + (6.32 \times 10^{-4})$ with $R^2 = 0.98$.

Fig. 2: The positive linear relationship among EC and Ionic strength of river and groundwater samples

Correlations Among Ions

Correlation and Principal Component Analysis (PCA) was carried out to understand the variance, proximity and relationship of cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+} , Ba^{2+}), anions (HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , F^-) and hydro-chemical parameters (pH, TDS and EC). Major

cations of river water sample shows moderate correlation with pH ($r^2 \sim 0.4$), whereas, anions are negatively correlated to pH. In the river, Sr shows the positive correlation with pH ($r^2 \sim 0.6$). Control of pH on chemical weathering is insignificant with respect to major alkaline earth elements; however it shows low positive correlation. Nonetheless, Na shows strong correlations with alkaline earth metals and negative correlation to potassium (K). Na shows positive correlations with bicarbonate ($r^2 \sim 0.8$), which possibly indicates the breakdown of plagioclase in the presence of carbonic acid. The possible chemical reaction resulting to produce kaolinite as a secondary product with Na^+ , HCO_3^- and silicic acid. Bicarbonate shows strong positive correlations with major cations (including Ba^{2+} and Sr^{2+}), excluding to potassium ($r^2 \sim 0.007$). All major cations are strongly correlated to each other, Mg^{2+} and Ca^{2+} shows significantly correlated except to the potassium (K^+). In the groundwater, nitrate does not show any correlations with pH, however, Cl^- , F^- and Na^+ ions show strong correlation with pH. Alkaline earth elements is strongly correlated with SO_4^{2-} . Bicarbonate in groundwater shows positive correlations to Ca^{2+} , Ba^{2+} and Sr^{2+} ions.

Discussion

Rock-Water Interaction and Ionic Acquisitions

The atmospheric contribution towards dissolve species in the river water considered as important source of ions (Pattanaik *et al.*, 2007 and 2013). After evapotranspiration loss, rainwater is percolated through soil and followed by the rock/sediments and finally reaches aquifer. During this process and subsequent interaction within aquifer, ions are enriched in the groundwater. Therefore observed TDS in the groundwater is higher compared to river water and it also indicates the longer rock-water interaction within the sub-surface zone. In terms of the hydrogeological processes, the dynamic of weathering and ion exchange process within sub-surface zone is active. Dominance of bicarbonate ion in river and groundwater systems, indicate that the protons are mainly from the carbonation process. The availability of soil carbon dioxide and dissolved atmospheric CO_2 might have played a major role in producing protons. Presence of intertrapeans within the Rajmahal basalt, possibly one of the source for SO_4^{2-} both in river and

groundwater samples. At the time of fieldwork, intertrapeans and tiny coal beds were observed in few outcrops. During chemical weathering, oxidation of sulphide minerals like pyrites may release SO_4^{2-} to the natural waters (Chakraborty *et al.*, 2015). Fertilizers used in the agricultural land along the river bank are another source of the anion such as NO_3^- and SO_4^{2-} in the river water. As the flow in this river is lien throughout the year except monsoon and post monsoon period, dilution effect does not play a major role for the ionic concentration. However, role of evaporation on the ionic budget needs to be estimated separately.

The hydro-geochemical facies and average ratio of $\text{HCO}_3^-/(\text{HCO}_3^- + \text{SO}_4^{2-})$ is ~ 0.99 , indicating dominance of carbonic acid during chemical weathering in the catchment area (Pandey *et al.*, 2001). River and groundwater constituents are related as $\text{Ca}^{2+} + \text{Mg}^{2+} > \text{Na}^+ + \text{K}^+$ and $\text{CO}_3^{2-} + \text{HCO}_3^- > \text{SO}_4^{2-} + \text{Cl}^-$ in respect to their chemical concentrations and occupies Ca^{2+} - Mg^{2+} - HCO_3^- hydrochemical facies as per Piper and Chadha's classification. As per the Chadha's classification (Chadha, 1999), river water samples and one groundwater (GW4) collected from the Gumani river shows similar trend (Fig. 3). In case of GW3 it plot in the boundary line of NaHCO_3 and Ca^{2+} - Mg^{2+} - HCO_3^- types. In case of the groundwater samples, it suggests the process of reverse cation exchange reaction or simple mixing processes which are active in the subsurface.

Constituents of alkali are relatively lower as compared to the alkaline earths. The average

Fig. 3: Hydrochemical facies as per the Chadha's classification. Water samples are plotted in the Ca^{2+} - Mg^{2+} - HCO_3^- field

contribution of alkaline earth (Mg+Ca) is 76% in the river water samples among total cations. Further, dominance of bicarbonate along with Mg+Ca in river water suggests the coupled reactions that are undergoing in the catchment area. As separate carbonates litho units are not reported from the study area, chemical weathering of calcite and other carbonate minerals present in the vesicles and amygdaloidal; and Ca-Mg bearing silicate minerals present in the Rajmahal basalt are major source of Ca+Mg and bicarbonate. The major constituents of Rajmahal basalt are plagioclase (commonly labradoritic and andesine), pyroxene (augite, pigeonite and rarely enstatite) and olivine minerals (Mukherjee, 1971; Kisku, 2020), hence dissociation of these primary minerals mainly control the river water chemistry. Concentration of these cations are dominated in the upper reach of the Morang river and tributaries compare to sample collected from the lower reach. Positive correlation ($R^2=0.9$) of Ca and Mg molar concentration shows common source of these cations. The average Ca/Mg molar ratio is 0.73 (range from 0.51 to 0.88) observed in the river water samples, which is similar to the ratio measured in the top layers of weathering profile developed over Rajmahal Basalt, whereas in the fresh basalt this ratio is ~ 2.9 (Kisku, 2020). This dominance of Mg over Ca in river water samples indicate either preferential weathering of Mg-bearing minerals or removal of Ca from the river water. Other possibility of incongruent weathering of Ca-Mg bearing minerals is unlike as

mobility of Ca is higher compare to Mg. Petrographic analysis of weathered basalt of Rajmahal shows Mg rich pyroxenes are more weathered compare to plagioclases (Kisku, 2020), which support the higher Mg content in the river water. Among four groundwater samples two shows Ca/Mg ratio close to one and other two shows higher ratio. The average ratio is 1.35 (ranging from 0.94 to 2.38) indicating higher rock-water interaction and dissolution of primary minerals. Alkali metals like Na marginally dominant towards lower reach of Morang river. Ratio between Na/Cl in river water samples are greater than one. Considering the evapotranspiration loss and atmospheric contribution of Cl⁻ in the absence of saline soil/evaporates, excess Na indicates silicate weathering. Primary mineral plagioclase present in the basalt and secondary minerals present in the voids are the major source of Na in the catchment area (Maybeck, 1987).

River water samples shows dominance of silicate weathering based on the Na normalized (Ca/Na and Mg/Na) bivariate plots (Figs. 4A and B). These ions are not corrected for the atmospheric contributions; however, as the Cl concentration is much lower compared to the other cations, the correction will not change the inference drawn from this plot significantly. Along with the water samples, three basalt samples analyzed during this study (complete analysis is not reported here) were also plotted to comprehend the contribution from basalt weathering.

Fig. 4: (A) Molar ratio plot of Ca/Na vs. Mg/Na of river and groundwater sample plots closer to silicate field. Three samples of basalt incorporated, which plots around scatter of water samples, (B) Similarly Na normalized bicarbonate and Ca show sample plots near to silicate field

Plot of HCO_3/Na vs. Ca/Na shows, samples are plotted close to the silicate field. It is inferred that the contribution from the basalt dissolution is the major source of ions in the catchment area.

Partial Pressure ($p\text{CO}_2$) in Water System

For calculation of $p\text{CO}_2$, equilibrium constants $K_{\text{CO}_2} = 10^{-1.47}$ and $K_1 = 10^{-6.35}$ at 25°C (Garrels and Christ, 1965) was used. The average temperature of the samples is $\sim 26^\circ\text{C}$. Calculated $p\text{CO}_2$ of the river water samples ranges from $10^{-3.15}$ – $10^{-2.67}$, whereas groundwater ranges to $10^{-1.59}$ – $10^{-1.09}$, and these values were higher than the atmospheric $p\text{CO}_2$ of $10^{-3.5}$. The higher values of $p\text{CO}_2$ in river water are a common trend, which indicates that the river water is out of equilibrium with atmospheric $p\text{CO}_2$ (Garrels and Mackenzie, 1971). Higher values of $p\text{CO}_2$ as compared to the atmospheric CO_2 indicates the extensive interaction of river water with soil CO_2 and these reaction continues till the equilibrium state achieves. Organic matter present in the soil act as additional source of CO_2 for water percolating through it and it can carry high amount of CO_2 as $p\text{CO}_2$ in soil could be nearly 10^{-2} (Singh, 1997). Contribution from soil CO_2 is supported by the moderate to dense vegetation cover found in the study area and the soil is adequately rich with organic matter. Furthermore, the excess $p\text{CO}_2$ in the river sample also suggest that the rate of re-equilibrium with atmosphere by liberating excess CO_2 is relatively low

as compared to the rate of solubility of CO_2 gas (Holland, 1978; Stumm and Morgan, 1981). Generally, increase in pH of water decreases the dissolved CO_2 , bivariate plot of pH to $p\text{CO}_2$ also shows the similar trend (Fig. 5). The elevated results in $p\text{CO}_2$ for groundwater indicate the continuous soil CO_2 interaction during infiltration. For comparison, $p\text{CO}_2$ was calculated from water draining Deccan volcanic province (DVP) and result shows similar trends, where few samples were attaining the equilibrium with the atmospheric CO_2 . Region with thin weathered mantle, absence of vegetation and long exchange with atmospheric CO_2 will facilitate the natural water to have identical value of atmospheric $p\text{CO}_2$. The carbonate dissolution process facilitated by the dissolved CO_2 with the water in the form of carbonic acid and protons.

Solubility Index (SI) and Mineral Precipitations

The solubility index (SI) of silica, sulphate and carbonate minerals (Table 2) were calculated using $\text{SI} = \log (\text{IAP}/K_{\text{eq}})$, where the IAP is “ionic activity product” and K_{eq} is equilibrium constant (Faure, 1998). In which, $\text{SI} > 0.5$ represents supersaturated, $\text{SI} < -0.5$ is undersaturated, and $\text{SI} = 0 \pm 0.5$ is near saturation. This saturation index will provide an indication of probable mineral precipitation, as mere saturation does not endorse the same. Mineral precipitation from natural solution depends up on the various controlling parameters other than saturation. However, SI for different carbonate minerals and percentage of samples are falling under different category of saturations were calculated (Tables 2 and 3) to understand the possible sink of cations in the river water. Sample collected from RW16 and RW21 (tributary samples) are supersaturated to dolomite (SID) and RW 16 shows supersaturated with respect to calcite (SIC). Most of the Morang river water samples either clustered within the near saturation level or under saturation for SID and SIC (Table 2, Fig. 6A). Similarly, SI of Aragonite (SIA) and Viterite (SIV), all the samples shows either near saturation or under saturation (Fig. 6B). Dolomite precipitation is a complex processes and generally does not occur readily in the saturated natural water. Although the rock-water interaction time is more in case of the groundwater samples, the saturation index for carbonate minerals were under saturation condition. The DVP river water samples (Dessert *et al.*, 2001)

Fig. 5: Negative trend indicates the increase of pH reduce the $p\text{CO}_2$. Samples of Rajmahal and DVP (Dessert *et al.*, 2001) are showing similar trend

Table 2: Indicating the Ionic activities, strength, saturation indices of carbonate (SID: Dolomite, SIC: Calcite, SIA: Aragonite, SIV: Viterite, SIG: Gypsum, SIB: Barite, SIAS: Amorphous Silica, and Quartz), H^+ activity and log Si in form of silicic acid. Whereas A: $-\log [K^+]/[H^+]$, B: $-\log [Na^+]/[H^+]$, C: $-\log [Ca^{2+}]/[H^+]^2$, D: $-\log [Mg^{2+}]/[H^+]^2$, E: $-\log [Ca^{2+}]/[Mg^{2+}]$ and F: $-\log P_{CO_2}$

	Sample	a+	a-	I	SID	SIC	SIA	SIV	SIG	SIB	SIAS	SIQ	H^+	logSi	p_{CO_2}	A	B	C	D	E
Morang River	RW1	6.3x10 ⁻⁰⁴	1.90x10 ⁻⁰³	2.19x10 ⁻⁰³	-0.47	-0.17	-0.31	-0.74	-4.34	-2.31	0.06	2.33x10 ⁻⁰³	7.41x10 ⁻⁰⁹	-3.97	-3.03	3.57	4.56	12.63	12.56	0.07
	RW10	6.74x10 ⁻⁰⁴	2.24x10 ⁻⁰³	2.47x10 ⁻⁰³	-0.23	-0.05	-0.20	-0.62	-4.23	-2.03	0.04	1.56x10 ⁻⁰³	7.08x10 ⁻⁰⁹	-4.15	-2.97	3.68	4.60	12.69	12.63	0.06
	RW2	6.12x10 ⁻⁰⁴	2.34x10 ⁻⁰³	2.43x10 ⁻⁰³	-0.52	-0.23	-0.37	-0.79	-4.32	-2.06	0.05	1.88x10 ⁻⁰³	9.77x10 ⁻⁰⁹	-4.07	-2.81	3.13	4.44	12.35	12.34	0.01
	RW13	4.34x10 ⁻⁰⁴	1.56x10 ⁻⁰³	1.58x10 ⁻⁰³	-1.61	-0.84	-0.99	-1.41	-4.43	-1.94	0.03	1.09x10 ⁻⁰³	1.35x10 ⁻⁰⁸	-4.30	-2.86	3.54	4.15	11.78	11.91	-0.14
	RW4	6.44x10 ⁻⁰⁴	2.39x10 ⁻⁰³	2.52x10 ⁻⁰³	-0.28	-0.09	-0.23	-0.65	-4.33	-2.10	0.05	2.12x10 ⁻⁰³	7.94x10 ⁻⁰⁹	-4.01	-2.89	3.27	4.55	12.57	12.53	0.04
	RW9	6.00x10 ⁻⁰⁴	2.46x10 ⁻⁰³	2.44x10 ⁻⁰³	-0.27	-0.13	-0.27	-0.70	-4.21	-1.88	0.06	2.41x10 ⁻⁰³	7.08x10 ⁻⁰⁹	-3.96	-2.93	3.55	4.59	12.57	12.62	-0.05
	RW7	5.81x10 ⁻⁰⁴	1.80x10 ⁻⁰³	2.03x10 ⁻⁰³	-0.83	-0.39	-0.53	-0.95	-4.21	-1.91	0.03	1.19x10 ⁻⁰³	9.55x10 ⁻⁰⁹	-4.27	-2.94	3.41	4.43	12.33	12.33	0.00
	RW6	6.64x10 ⁻⁰⁴	2.09x10 ⁻⁰³	2.34x10 ⁻⁰³	-0.60	-0.25	-0.39	-0.81	-4.09	-1.83	0.05	1.80x10 ⁻⁰³	9.55x10 ⁻⁰⁹	-4.09	-2.88	3.46	4.50	12.40	12.36	0.04
	RW18	7.41x10 ⁻⁰⁴	2.27x10 ⁻⁰³	2.54x10 ⁻⁰³	-0.33	-0.14	-0.29	-0.71	-3.85	-1.50	bdl	00	7.94x10 ⁻⁰⁹	bdl	-2.92	3.93	4.61	12.55	12.57	-0.01
	RW17	6.41x10 ⁻⁰⁴	2.26x10 ⁻⁰³	2.31x10 ⁻⁰³	-0.66	-0.31	-0.46	-0.88	-4.15	-1.75	0.07	2.67x10 ⁻⁰³	9.55x10 ⁻⁰⁹	-3.91	-2.84	3.72	4.51	12.30	12.32	-0.03
Tributaries (Morang R.)	RW22	7.50x10 ⁻⁰⁴	2.44x10 ⁻⁰³	2.52x10 ⁻⁰³	-0.84	-0.41	-0.56	-0.98	-4.06	-1.56	0.06	2.25x10 ⁻⁰³	1.32x10 ⁻⁰⁸	-3.99	-2.67	3.76	4.47	12.03	12.08	-0.05
	RW5	6.28x10 ⁻⁰⁴	2.00x10 ⁻⁰³	2.27x10 ⁻⁰³	-0.40	-0.13	-0.28	-0.70	-4.36	-2.19	0.05	2.10x10 ⁻⁰³	7.41x10 ⁻⁰⁹	-4.02	-3.00	3.48	4.55	12.64	12.57	0.07
	RW3	8.58x10 ⁻⁰⁴	3.70x10 ⁻⁰³	4.07x10 ⁻⁰³	-0.24	-0.08	-0.23	-0.65	-2.68	-0.44	0.04	1.61x10 ⁻⁰³	9.77x10 ⁻⁰⁹	-4.13	-2.77	3.46	4.62	12.46	12.45	0.01
	RW12	7.06x10 ⁻⁰⁴	2.07x10 ⁻⁰³	2.47x10 ⁻⁰³	-0.63	-0.25	-0.40	-0.82	-3.88	-1.74	0.06	2.21x10 ⁻⁰³	1.10x10 ⁻⁰⁸	-4.00	-2.82	3.67	4.40	12.34	12.27	0.06
	RW8	9.86x10 ⁻⁰⁴	3.24x10 ⁻⁰³	3.70x10 ⁻⁰³	0.21	0.16	0.01	-0.41	-3.93	-1.52	0.04	1.71x10 ⁻⁰³	9.33x10 ⁻⁰⁹	-4.11	-2.68	3.50	4.66	12.62	12.57	0.05
	RW11	6.81x10 ⁻⁰⁴	2.13x10 ⁻⁰³	2.35x10 ⁻⁰³	-0.48	-0.19	-0.33	-0.76	-4.07	-1.80	0.05	1.82x10 ⁻⁰³	8.32x10 ⁻⁰⁹	-4.08	-2.93	3.81	4.56	12.51	12.47	0.04
	RW20	5.18x10 ⁻⁰⁴	2.06x10 ⁻⁰³	2.04x10 ⁻⁰³	-0.79	-0.44	-0.58	-1.00	-4.26	-1.81	0.06	2.58x10 ⁻⁰³	8.71x10 ⁻⁰⁹	-3.93	-2.92	3.53	4.44	12.25	12.39	-0.14
	RW21	1.13x10 ⁻⁰³	3.54x10 ⁻⁰³	3.87x10 ⁻⁰³	0.85	0.49	0.34	-0.08	-3.94	-1.67	0.03	1.36x10 ⁻⁰³	4.57x10 ⁻⁰⁹	-4.21	-2.96	4.07	5.11	13.22	13.16	0.06
Groundwater (Gumani R.)	RW19	9.62x10 ⁻⁰⁴	2.42x10 ⁻⁰³	2.99x10 ⁻⁰³	0.25	0.14	0.00	-0.42	-3.86	-1.70	0.02	9.10x10 ⁻⁰⁴	5.50x10 ⁻⁰⁹	-4.38	-3.05	3.74	4.96	12.97	12.98	-0.02
	RW15	6.07x10 ⁻⁰⁴	2.13x10 ⁻⁰³	2.21x10 ⁻⁰³	-0.17	-0.09	-0.24	-0.66	-4.11	-1.74	0.04	1.65x10 ⁻⁰³	5.01x10 ⁻⁰⁹	-4.12	-3.15	3.81	4.77	12.82	12.90	-0.08
	RW14	5.90x10 ⁻⁰⁴	2.20x10 ⁻⁰³	2.23x10 ⁻⁰³	-0.45	-0.22	-0.36	-0.78	-4.14	-1.74	0.03	1.32x10 ⁻⁰³	7.08x10 ⁻⁰⁹	-4.22	-2.98	3.60	4.60	12.53	12.58	-0.05
	RW16	1.09x10 ⁻⁰³	3.29x10 ⁻⁰³	3.85x10 ⁻⁰³	0.92	0.53	0.38	-0.04	-3.81	-1.69	0.04	1.75x10 ⁻⁰³	4.37x10 ⁻⁰⁹	-4.10	-3.01	4.01	5.05	13.31	13.24	0.07
	GW1	1.84x10 ⁻⁰³	4.34x10 ⁻⁰³	5.78x10 ⁻⁰³	-2.48	-1.16	-1.30	-1.73	-3.01	-2.16	0.11	4.47x10 ⁻⁰³	2.82x10 ⁻⁰⁷	-3.69	-1.25	1.87	3.56	9.87	9.77	0.10
	GW2	2.44x10 ⁻⁰³	5.54x10 ⁻⁰³	2.61x10 ⁻⁰³	-1.50	-0.63	-0.78	-1.20	-2.45	-0.69	0.10	3.91x10 ⁻⁰³	2.04 x10 ⁻⁰⁷	-3.75	-1.17	2.21	3.80	10.32	10.15	0.17
	GW3	1.81x10 ⁻⁰³	4.32x10 ⁻⁰³	1.58x10 ⁻⁰³	-2.25	-0.84	-0.98	-1.40	-3.23	-2.15	0.09	3.67x10 ⁻⁰³	1.15 x10 ⁻⁰⁷	-3.78	-1.59	2.30	4.09	10.53	10.02	0.51
	GW4	1.60x10 ⁻⁰³	4.11x10 ⁻⁰³	4.07x10 ⁻⁰³	-2.42	-1.11	-1.26	-1.68	-3.42	-2.77	0.17	6.63x10 ⁻⁰³	2.82 x10 ⁻⁰⁷	-3.52	-1.09	1.27	3.56	9.76	9.63	0.13

Fig. 6: (A) Saturation index of calcite (SIC) and dolomite (SID) plotted for river water and ground water of Rajmahal tributaries with DVP drainage, (B) Similar plot for Saturation index of vaterite (SIV) and aragonite (SIA)

shows SI of dolomite and calcite ranges from nearly -2 to +3 and -1 to +1.53 respectively. Which shows higher percentage of samples are falling in the supersaturated filled compared to the river draining Rajmahal basalt (Fig. 6A and B). Similar relation is also observed for the SIV and SIA. Saturation index for gypsum (SIG) and barite (SIB) is calculated and result shows river samples are in under saturation (Table 2). Groundwater samples show marginally higher value of SIG compared to river water, however all the water sample shows similar SIB value except one ground water sample collected from GW2. Paragenetic sequence during evaporite deposits shows precipitation of gypsum follows the calcite. However, precipitation of gypsum and barite from river water is rare compared to calcite.

The concentration of silica in the river water varies from 42 to 122 ($\mu\text{mole/l}$) and groundwater shows a range of 167-303 ($\mu\text{mole/l}$). Silica in the form of silicic acid (H_4SiO_4) in natural water is essentially derived from the dissolution of common rock forming silicate minerals like feldspar, pyroxene, olivine and amorphous silica. Quartz is sparingly soluble in natural water and required longer rock-water interaction periods, whereas, amorphous silica is reactive and maintains equilibrium with H_4SiO_4 . Glass, secondary silica and colloidal silica in the void of the Rajmahal basalt is reported (Mukherjee, 1971), which can be easily dissociated during chemical weathering. The

SiO_2 dissolution reaction for amorphous silica and quartz is expressed as $\text{SiO}_2 (\text{amorphous silica/quartz}) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$. The Saturation Index of amorphous silica (SIAS) and quartz (SIQ) was calculated as $\text{SI}_{(\text{SIAS}/\text{SIQ})} = \log [\text{H}_4\text{SiO}_4] / K_{(\text{SIAS}/\text{SIQ})}$, where, K - equilibrium constants at 25°C for SiO_2 or amorphous silica (Faure, 1998). The activity of silicic acid $[\text{H}_4\text{SiO}_4]$ for river water samples mostly clustered within -4.5 to -3.9, whereas groundwater samples are in the range from -4.0 to -3.5. The river draining DVP shows activity of H_4SiO_4 ranged from -4.5 to -3.4 (Fig. 7A), the maximum SIAS (~ 0.21) and SIQ (0.02) indicates the high values as compared to the Rajmahal drainage system (Table 2). Dissolution of amorphous silica or silicate minerals in river water is relatively high in DVP draining river indicating intense weathering compared to Rajmahal basalt. Though, the river water of both the provinces is showing the limited solubility, the activity of silicic acid is significantly low. Therefore, the SIAS and SIQ shows certainly no precipitation as the activity of silicic acid is also doesn't increases above the required value of equilibrium (-2.74) in the reaction. Low values of silicic acid activity in the water samples can be observed with their solubility index (Fig. 7A). Silicic acid activity is being compared to the pH in river water, in general the activity of silicic acid increases as lowering in pH (in acidic condition) values (Fig. 7B). Lowering in pH causes to dissociate silicates and give rise to silicic acid in water. The activity of silicic acid in DVP is high as compared to

Fig. 7: (A) Saturation index of amorphous silica with respect to the silicic acid activity in river and groundwater samples, (B) Silicic acid activity with respect to pH of river and groundwater samples

Table 3: Percentage (%) of minerals indicating the saturation level in RW: River water and GW: Groundwater. (*n*: total number of samples)

Type	Level	<i>n</i>	SID	SIC	SIA	SIV	SIG	SIB
RW	Near saturation (0 ± 0.5)	22	54.5	90.9	81.8	18.2	0.0	4.5
	Under saturation (< -0.5)		36.4	4.5	18.2	81.8	100.0	95.5
	Over saturation ($> +0.5$)		9.1	4.5	0.0	0.0	0.0	0.0
GW	Under saturation (< -0.5)	4	100	100	100	100	100	100

the river water sample collected from Rajmahal. As reported from DVP (Dessert *et al.*, 2001), intense chemical weathering under tropical climatic condition lead to this higher value. The low activity of silicic acid in water may possibly reflect a slow rate of dissolution to the silicate minerals during chemical weathering.

Mineral Equilibria

Thermodynamic studies of natural solution and its equilibrium with respect to different mineral phases helps to understand the probable transformation to other stable phases at a given physico-chemical environment (Garrels and Christ, 1965; Stumm and Morgan, 1981). This transformation may be breakdown of existing phases or neoformation or precipitation from a saturated solution. Due to the dissolution of minerals in natural water, the constituent present in the solution helps to understand the weathering processes active in that region. Major ion composition of water and suspended sediments in the

river reflects the mineralogical composition of the host rock and the nature of chemical weathering is active in the catchment area. This also helps to theoretically predict the stability of minerals at certain geochemical environmental conditions. The law of mass action, relationship between standard free energy changes of a reaction and their equilibrium constant, the mineral stability field were established for river water draining over Rajmahal and compared with river draining DVP. The predictable state of stability from muscovite to kaolinite, microcline to kaolinite, and pyrophyllite to kaolinite, conversion phase at 25° C of water sample at 1 atm. pressure was estimated based on the expression described by the Faure, 1998; Helgeson, 1969. In this system, activity ratio of ($\log [K^+]/[H^+]$ vs. $\log [H_4SiO_4]$) for river and groundwater were mostly occupied within the field of kaolinite and two samples of the river water are onto the boundary line of kaolinite to muscovite field and possibly indicates the presence of illite (also includes to the K-smectite and pyrophyllite), whereas sample from DVP occupies

Fig. 8: (A) Both river and groundwater sample shows in the kaolinite field, whereas, DVP samples extent towards muscovite field. With respect to (B) albite and (C) anorthite samples from the Rajmahal river water is in equilibrium with

Figure caption continued to next page

kaolinite, whereas some samples of DVP are occupied in the calcite field, (D) Solubility limits of pure Mg-silicates, each of the minerals represented are dissolves in solution where $[\text{Mg}^{2+}]/[\text{H}^+]^2$ ratio activity of silicic acid are less than those of their respective solubility lines and (E) transformation of Mg silicates into secondary minerals and (F) Stability field diagram for kaolinite, Ca-smectite and Mg-smectite in coordination to $[\text{Ca}^{2+}]/[\text{H}^+]^2$ and $[\text{Mg}^{2+}]/[\text{H}^+]^2$, sample plots almost parallel to the boundary line between Ca and Mg-smectite indicating cation exchanges process

the muscovite and microcline (Fig. 8A). The albite and anorthite system (Na and Ca) for river water samples occupied to kaolinite for both the provinces, indicates the equilibrium condition with kaolinite and possibly these primary minerals are converted to secondary minerals dominantly as kaolinite (Figs. 8B and C).

Similarly samples occupy the kaolinite field in Mg-silicate stability diagram. $[\text{Mg}^{2+}]/[\text{H}^+]$ ratio in magnesite effectively limits for natural solution to the value less than $10^{13.52}$, indicated with the dotted line (Fig. 8D). The Mg bearing mineral dissolves congruently, consequently releases Mg ions and silicic acid in natural solution. Stabilities for Mg bearing minerals are limited by the activities of Mg^{2+} , H^+ , and silicic acid with which normally get associated naturally (Faure, 1998). The river water samples are reaching close to the Mg-chlorite boundary, in which some of DVP river samples are also in stable at Mg-chlorite and magnesite field (Fig. 8E). Adding other minerals to this stability diagram, water samples are within the natural solution, where some samples are extended towards anthophyllite (Fig. 8D). In the stability diagram of $\log [\text{Ca}^{2+}]/[\text{H}^+]^2$ and $\log [\text{Mg}^{2+}]/[\text{H}^+]^2$ explaining the reaction involved in kaolinite to chlorite transformation (Faure, 1998; Helgeson, 1969), the river water occupies the Ca-smectite, whereas groundwater are within the kaolinite field (Fig. 8F). The Ca-Mg activity in the river water samples are almost collinear and parallel to the Ca-smectite and Mg-smectite boundary line indicating the cation exchange process. Presence of kaolinite, smectite, palagonite and mixed layer clay have been reported from the petrographic and powdered XRD analysis of fresh and weathered basalt of Rajmahal (Sarbadhikar, 1966; Mukherjee, 1971; Kisku, 2020), which support the inference drawn from the mineral equilibrium analysis.

Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was applied to minimize the multidimensional variables and shows

the pattern suitably associated to the different geochemical processes. The highest eigen values were observed in the first three principal component numbers as shown in the scree plot (PCA1, PCA2 and PCA3). As the numbers of parameters were 14, total fourteen components were calculated to observe the variations. It is not necessary to include all principal components (PC's), essentially PC's with high Eigen are used. However, in this study first two components (PCA1 and PCA2) were used where Eigen values are significant and maximum. In terms of eigen values for this study, the river water samples shows gradual decrease and groundwater samples are almost constant from fourth component numbers (Fig. 9). Hence, two components (PCA1 and PCA2) for river and groundwater are interpreted. In river water samples, the anions and cations are closely associated to each other (Figs. 10A and B). The coefficient of Principle Components (PC) of river water sample in PCA1 is positive for Ca^{2+} , Mg^{2+} , Na^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , F^- , Sr^{2+} , Ba^{2+} , TDS, EC and pH, except for potassium. Whereas in PCA2, the coefficients of PC's are positive for SO_4^{2-} , Cl^- , NO_3^- , F^- and remaining parameters shows negative coefficients. The positive coefficients of PC's for PCA3 is observed for Mg^{2+} , Na^+ , HCO_3^- , SO_4^{2-} , Cl^- , F^- , Ba^{2+} , TDS and EC, whereas, other parameters shows negative coefficients. The coefficients of PC's for Mg^{2+} , Na^+ , HCO_3^- , NO_3^- , F^- , Ba^{2+} , TDS, EC are positive in either two PC's, whereas for SO_4^{2-} , Cl^- and F^- shows positive for all three PC's. Anions like SO_4^{2-} , Cl^- and F^- , shows good positive coefficient and possibly indicates the same source. Potassium behaves differently in PCA analysis may be due to the lower abundance of K-feldspars in the basalt and its behavior after releasing from the primary minerals. It gets easily accommodated within the clay minerals after being removed from the primary minerals, therefore concentration of K in the natural water needs to be evaluated carefully. Major cations are grouped to the physical parameter such as TDS and EC, these parameters are dominant by the ions such as Ca^{2+} , Mg^{2+} , Na^+ , Ba^{2+} and Sr^{2+} . Similarly, highest Eigen

Fig. 9: Scree plot of physical parameter and geochemical composition for river and groundwater samples, indicating significantly high eigen values in first three principal component numbers (PC1, PC2 and PC3)

Fig. 10: PCA analysis of river water samples for various physical parameters and chemical composition of (A) river water and (B) groundwater

values were observed in PCA1 and PCA2 for groundwater samples. The coefficient of PC's for groundwater sample in PCA1 shows the positive value for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , F^- , Sr^{2+} , Ba^{2+} , TDS, EC and pH, except to the nitrate (NO_3^-). In PCA2 shows positive for Na^+ , K^+ , Cl^- , F^- and pH. Whereas, in PCA3 their coefficients are positive for Na^+ , K^+ , Cl^- , NO_3^- , Sr^{2+} , TDS, EC and pH. In PCA, Na^+ , Cl^- and F^- are closely associated, which indicate possibly these ions are having common sources in the groundwater. On other hand Ca^{2+} , Ba^{2+} , Sr^{2+} , is remarkably associated with bicarbonate and SO_4^{2-} ions. In river water as well as groundwater, behavior of NO_3^- is completely different than the other ions, where the coefficient of PC's for NO_3^- in PCA1 and PCA2 are negative (Fig. 10). The deviation of nitrate in PCA indicate that the source of NO_3^- is not related to the chemical weathering active in the catchment area and possibly derived from the anthropogenic sources. Spurious NO_3^- abundance in two groundwater sample is difficult to explain by this PCA analysis. Coefficients for Na^+ , K^+ , Cl^- and pH are positive in all three PC's indicating the control of salinity and pH of groundwater on these ions. Similarly the control of Ca^{2+} , Mg^{2+} , HCO_3^- , Sr^{2+} and Ba^{2+} ions on TDS and EC of groundwater can be inferred from PCA analysis. The behavior of Mg^{2+} and its association with other ions in the PCA analysis of river water and groundwater is different. In the river water PCA analysis indicate both Mg is associated with bicarbonate and close to Ca, indicating the same source and supporting the preferential dissolution of Ca-Mg bearing mineral like pyroxene. Similarly, the behavior of SO_4^{2-} in PCA analysis is different for groundwater and river water, reflecting separate processes are responsible for its concentration. Association of different ions and clustering does not support any significant evaporite and carbonate weathering in the study area. As inferred from the elemental ratio, the silicate weathering is dominant in the catchment area and contributing to the major ion composition of the river and groundwater. Carbonate weathering cannot be ruled out completely as various carbonate minerals are present in the vesicles and voids of the basalts.

Conclusions

Water samples collected from the upper reaches of Morang river shows higher Ca and Mg concentration

compared to lower reach where Na and K is dominant. Based on the Piper and Chadha's classifications, water samples collected from the river and groundwater is $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ hydrochemical types. In the Morang river catchment area, dissolution of primary minerals and secondary minerals present in the voids of basalt controls the ionic budget of the river. Contribution from Morang river does not control the ionic budget of Gumani river. Absence of major industrial area in the catchment area cannot rule out the anthropogenic contribution to the surface water. Unusual high NO_3^- concentration at places indicate the source of NO_3^- from the agricultural field located along the river. Higher values of $p\text{CO}_2$ ($>10^{-3.5}$) in water samples as compared to the atmospheric CO_2 , indicates the possible contribution from soil CO_2 and lower rate of re-equilibrium with atmosphere by releasing the excess of CO_2 . Most of the water samples are either under saturated or near saturation with respect to carbonates, except two river samples. Mineral stability diagram shows these samples are in equilibrium with kaolinite, indicating climate and adequate rainfall support the chemical weathering of primary minerals up to kaolinite. Based on the elemental ratio, correlation and Principle Component Analysis (PCA), it is inferred that a) silicate weathering is dominating in the study area b)

preferential weathering of pyroxene (augite and pigeonite) compared to plagioclase minerals leads to the low Ca/Mg ratio in river water; c) preferential weathering supported by the lower SIC value and petrographic study of weathered basalt; d) most of the cations are controlled by pH in river water, whereas some anions are controlled by pH in the groundwater. Further study on chemical weathering of Rajmahal basalt is required to understand its control on groundwater chemistry and the associated atmospheric CO_2 drawdown.

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