



Hydrogeochemical modelling to understand the surface water–groundwater interaction around a proposed uranium mining site

S MANOJ, M THIRUMURUGAN and L ELANGO*

Department of Geology, Anna University, Chennai, Tamil Nadu 600 025, India.

*Corresponding author. e-mail: elango34@hotmail.com

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The interaction between surface water and groundwater is a complex process and is considered as an important component for controlling the mining activities. The objective of this study is to understand the interaction between surface water and groundwater around a proposed uranium mining site by geochemical modelling. Surface water and groundwater samples along the groundwater flow path were collected from September 2013 to June 2016 across the uranium mineralised region located near Gogi, Karnataka, India. Collected water samples were analysed for major ion and uranium concentrations. This hydrochemical data was used as input in the geochemical modelling code PHREEQC to calculate the uranium speciation and saturation indices. Inverse geochemical modelling was performed along the flow direction by considering the mineralogical composition of host rock. Measurement of surface water and groundwater level indicates that the recharge and discharge of this region were primarily controlled by rainfall. Relation between the temporal variation of rainfall and saturation index of mineral reveals the various scenarios of interaction between surface water and groundwater around the mineralised region. Silicate/carbonate weathering, irrigation return flow and dissolution of evaporites are the major processes indicated by inverse geochemical modelling, which controls the hydrogeochemical evolution of water in this region. Geochemical modelling was effectively used to understand the temporal changes in the interaction between surface water and the groundwater in a uranium mineralised region.

Keywords. Uranium; Bhima basin; PHREEQC; geochemical speciation; saturation index; inverse modelling.

1. Introduction

Mineral exploitation plays a major role in world's economic and industrial development. It guarantees the continuous supply of raw materials to the construction and manufacturing sectors for the economic development of the country (Hein *et al.* 2004). Uranium is one such raw material, extracted through conventional mining and is used to generate nuclear energy. Due to rise in demand and depletion of existing uranium reserves, it becomes essential to find new deposits and also increase the

production of the existing deposits (Mason 2014). In general, mining of economic minerals induces significant changes in surface hydrology, groundwater systems and water quality (Booth 2006). Diversion of surface water, creation of additional ponds, changes in stream alignment, interaction between surface water and groundwater as well as changes in water quality are some of the challenges need to be addressed during mining (Kay *et al.* 2006). Vance *et al.* (2014) compared the currently leading approaches of managing environmental and health impacts of uranium mining

with the outdated practices which suggest that innovative, modern mining practices combined with strictly enforced regulatory standards will reduce the environmental and health risks caused due to mining.

Understanding the interaction between surface water and groundwater is one such essential step for the optimal management of regional water resources during mining operations. In mining areas, extra care was taken to maintain the quality as well as regional fluctuation in the water table to preserve the surface water and groundwater ecosystem (ANZECC 2000). The interaction of groundwater with adjoining lakes, reservoirs, streams and canals is the major aspect that governs the inflow, outflow and flow direction of the region. Numerous studies based on stable isotopes (Katz *et al.* 1997; Paces and Wurster 2014; Alahaho *et al.* 2015), hydrochemistry (Soulsby *et al.* 2005; Ayenew *et al.* 2008; Martinez *et al.* 2015) and modelling (Pahar and Dhar 2014; Voeckler *et al.* 2014; Hu *et al.* 2016; Yi *et al.* 2016) were widely applied to understand the surface water and groundwater interactions. Apart from these, hydrogeochemical evolution from surface water to groundwater through the unsaturated zone using inverse modelling have been carried out by various researchers (Lecomte *et al.* 2005; Federico *et al.* 2008; Sharif *et al.* 2008; Belkhiri *et al.* 2010) to understand the geochemical evolution of water and the process responsible for the evolution. Eary *et al.* (2003) also assessed the water quality changes in connection with the mining operations using the inverse modelling and Brindha and Elango (2014) have used the geochemical modelling to understand the geochemical changes in groundwater due to leaching from uranium tailing ponds.

Uranium exploration in India dates back from early 1950s and the deposits belongs to the Proterozoic age has been considered as the potential target (Chaki *et al.* 2005). Bhima basin is one among the seven Purana basins (Palaeoproterozoic–Neoproterozoic age) in Indian peninsula (Kale and Phansalkar 1991), which is characterised by seven major faults (Kale and Peshwa 1995) in which the medium grade of uranium deposits occurs around one of them (Achar *et al.* 2001). Investigations in the Bhima basin were carried out by an integrated approach with several exploration techniques was adopted and the extent of uranium reserve in this region was estimated (Achar *et al.* 2001). This uranium deposit is structurally controlled and of hydrothermal vein type (Chaki *et al.*

2011). To meet the increasing demand of uranium, it is planned to mine uranium ore from this area in future. Manoj *et al.* (2017a, b) assessed the concentration of uranium in groundwater of the entire Shahpur taluk which ranged from below determination level (<0.05 ppb) to 302 ppb.

Hydrogeochemical methods are commonly used to establish the relationship between the surface water and groundwater and the mechanism involved in the geochemical evolution. Hydrogeochemical methods based on the concentration of ions in water and saturation indices of minerals provide a cost-effective alternative to understand the groundwater recharge and flow processes over a large area. As this region with uranium deposit has two large lakes with complex hydrogeological setup, it is necessary to understand the interaction between the surface water and groundwater. In addition, this study will serve as the baseline data which will be helpful to assess the present and future impacts from mining that can possibly influence the hydrogeology and geochemistry of the surface water and groundwater of this region. Thus, the objective of this study is to understand the interaction between surface water and groundwater in the uranium mineralised Gogi region, Karnataka, India, by geochemical modelling.

2. Study area

The study area lies in the southern part of the Bhima basin, which is located around 12 km west of Shahpur, Yadgir district of Karnataka, India. The geographical extent of the study area is about 14 km² with 1571 houses and about 10,000 residents as per the 2011 census (Chandramouli and General 2011). The area experiences three seasons: (i) summer from late February to mid-June, (ii) southwest monsoon from mid-June to late September and (iii) dry winter until January, where the temperature ranges from 37° to 46°C, 25° to 37°C and 12° to 32°C, respectively (Karunakara *et al.* 2014). The average annual rainfall in this area is about 839 mm and most of the precipitation occurs during the southwest monsoon. The surface runoff resulted in the development of dendritic drainage pattern in this area. Two major lakes namely Melinakere (L1 lake) and Kelaginakere (L2 lake) are present in the upstream and downstream of the mineralised zones, respectively. These lakes support the water demand for domestic and agricultural purposes in the study area (figure 1).

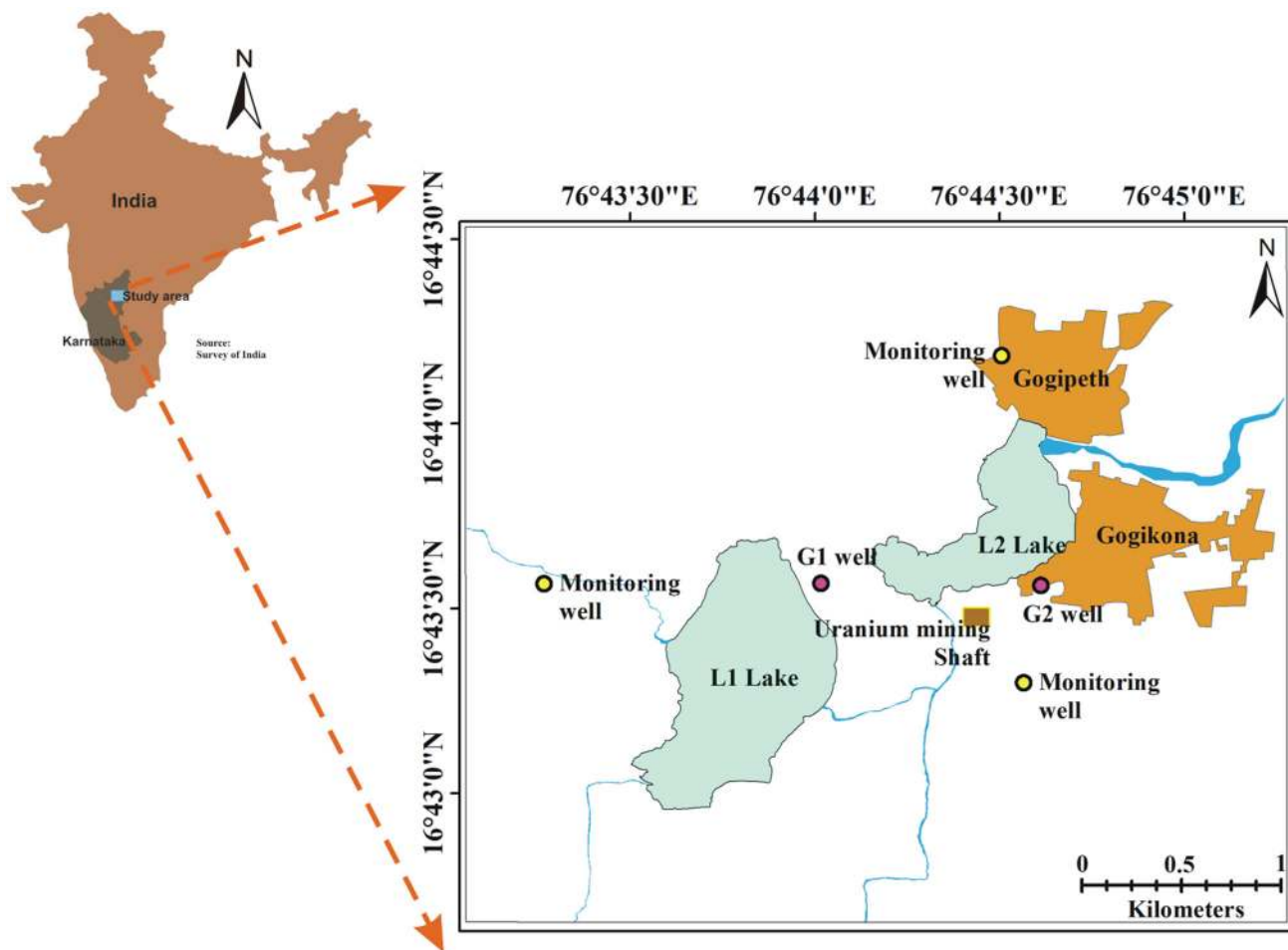


Figure 1. Study area.

The cropping pattern depends on three seasons namely kharif, rabi and summer. The kharif cropping season is from July to October during the southwest monsoon and the rabi cropping season is from October to March. The crops grown between March and June are summer crops. The crops covered in this area are kharif: paddy, jowar, tur, cotton, and sunflower; rabi: jowar, wheat and bengal gram; and summer: paddy and groundnut.

3. Uranium mineralisation and geology of Gogi region

In India, most of the uranium deposits fall under the low-grade category, which include the deposits in the states of Jharkhand, Chhattisgarh, Meghalaya, Andhra Pradesh, Rajasthan and Haryana. The Gogi uranium deposit in the state of Karnataka is of the higher quality (medium grade) among the ores found in the rest of the country (Chaki *et al.* 2011). Based on the available

lithologs, the cross-section along the Gogi uranium mineralised zone was arrived (figure 2). Uranium mineralisation in Gogi region occurs within the major E–W trending Gogi–Kurlagere fault (Karunakara *et al.* 2014), passing through the mineralised zone, which takes a NE swerve near the south of Gogi lake and attains easterly trend near the north of the Gogi village (Achar *et al.* 2001). Chaki *et al.* (2005) reported that the mineralisation is steeply dipping and the fault is reverse in nature. The strike of the reverse fault is N50°E–S50°W and is dipping towards S40°E. Intense brecciation in limestone, steeply dipping beds and basement granites are the characteristic features of the fault zone indicating the involvement of basement rocks during tectonisation. Uranium occurring in uraninite is hosted mainly in sheared phosphatic limestone, non-phosphatic limestone and basement granite present in this region. During the drilling by Atomic Mineral Directorate, the surface samples collected contain 0.017–0.084% and 0.02–0.27% of U₃O₈ in phosphatic and non-phosphatic

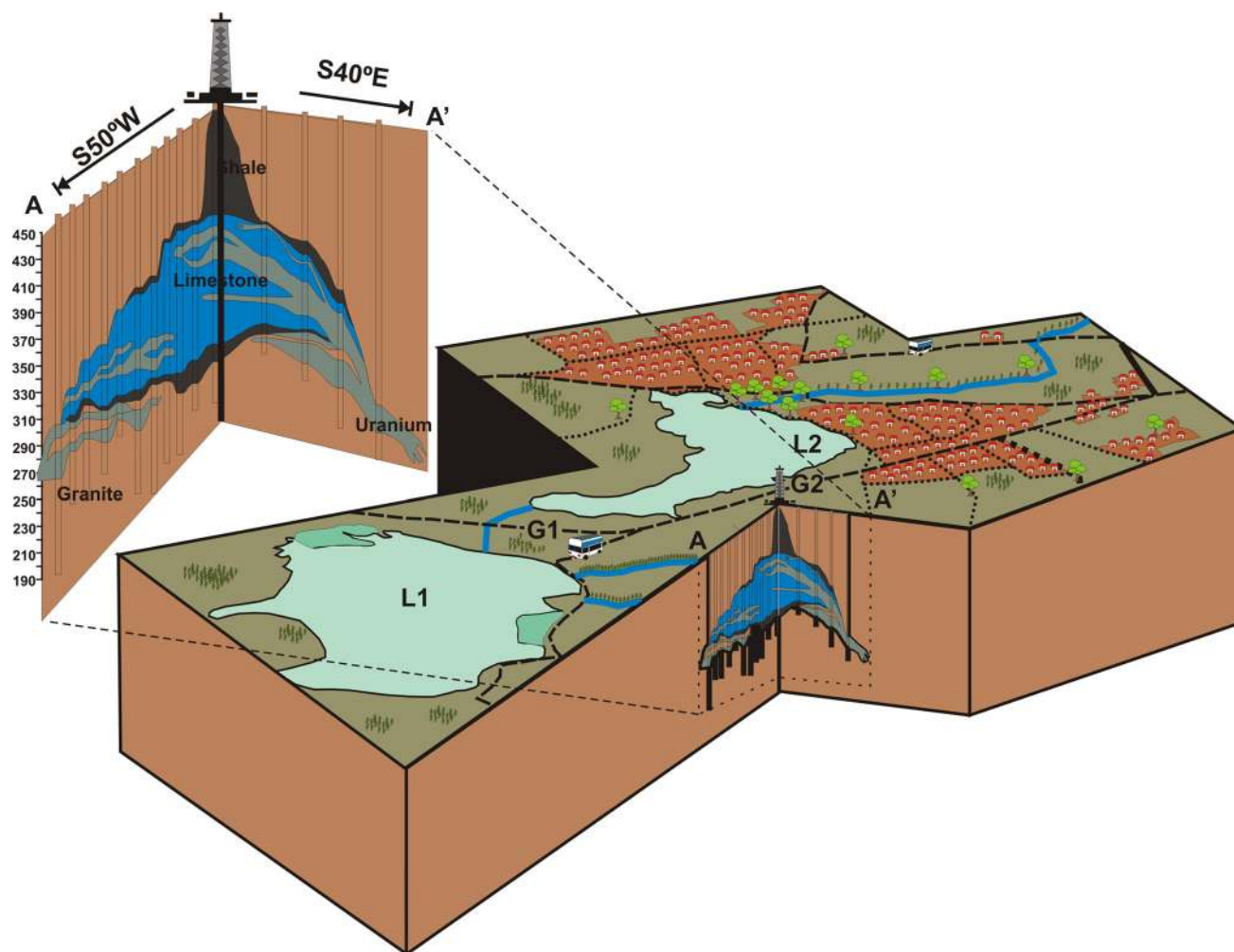


Figure 2. Cross-section across the uranium mineralised zone (after Chaki *et al.* 2005, 2011).

limestones, respectively, whereas some of the core samples of granitic terrain contain up to 20% of U_3O_8 (Chaki *et al.* 2005). Mineralisation in granite close to the unconformity contact shows radiometric assay of 0.02–0.3% U_3O_8 (Achar *et al.* 2001). Uranium in this region is apparently derived from hydrothermal leaching of basement granite rock and deposited in the fault zone near to the contact of carbonate rocks due to the favourable geochemical environment of uranium precipitation (Senthil and Srinivasan 2002).

4. Methodology

4.1 Sample collection

Surface water (L1 and L2) from the two lakes and groundwater (G1 and G2) from the nearby wells were collected so as to approximately represent the general groundwater flow direction (figure 2).

Water sampling was carried out once in 3 months from September 2013 to June 2016. Geologically, L1 and G1 fall in granitic terrain, whereas L2 and G2 fall in carbonate terrain. The aim and purpose of choosing this location is to understand the geochemical variation during the migration of water from granitic terrain to carbonate terrain. Collected water samples were filtered through $0.45\ \mu\text{m}$ and transferred to the laboratory for the analysis of major ions and uranium concentration.

4.2 Hydrogeochemical characterisation

The pH, electrical conductivity (EC), temperature and redox potential (Eh) of surface water and groundwater were measured in the field using portable multiparameter system (Eureka Sub Manta-2) and the concentrations of carbonate and bicarbonate were estimated using the Merck alkalinity test kit (111109). Cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (Cl^- , SO_4^- and NO_3^-) were

analysed in the laboratory from the filtered water samples using ion chromatograph (IC Metrohm 861). Ion balance error was calculated and was found to be within $\pm 10\%$. The concentration of uranium in water samples was analysed using a laser fluorimeter (Quantalase LF-2a). This method measures the fluorescence of uranium complex in the water sample by excitation under ultraviolet light. The fluorescence of uranium complexes is measured by a sensitive photomultiplier tube. The accuracy of analysis was achieved through the measurement of certified standard reference solution ICP-MS-66N and the precision was established by duplicate analysis of every two samples.

4.3 Measurement of surface water and groundwater levels

Water level fluctuation in surface water bodies, as well as subsurface, is a primary tool to understand the degree of interaction between surface water and groundwater. Aquifer system readily reacts to the changes that take place during the recharge and discharge of water with respect to time and season. In order to understand the mechanism of the interaction process, the water level in the lakes was measured using a scale fixed at a place with the known elevation and the groundwater level was measured during the sampling campaign using the water level indicator (Solinst 101) in the wells (G1 and G2) adjacent to the lakes and in three more wells located around the mineralised zone. Based on the measured surface water and groundwater level, groundwater table map was prepared using ArcGIS 10.1 software for different time periods.

5. Geochemical modelling

5.1 Species calculation and saturation index

Uranium occurs as U^{4+} , U^{5+} and U^{6+} ion in natural water; however, from geochemical point of view, the oxidation states of U^{4+} and U^{6+} ions were dominant (Dongarra 1984). U^{4+} occurs in the form of hydroxides, hydrated fluorides and phosphates, whereas U^{6+} is the most stable state occurring in the form of U_3O_8 (uraninite). The distribution of aqueous uranium species in surface water and groundwater of this region was calculated based on geochemical data using PHREEQC (Parkhurst 1995). Temperature, pH, Eh, and concentrations of ions are the essential data used as an input for the species calculation.

The saturation index (SI) was applied to predict the reactive mineralogy of the subsurface from the groundwater sample data without collecting the samples of the solid phase (Rajmohan and Elango 2004). The SI was calculated using the computer geochemical program PHREEQC for surface water and groundwater samples. It is defined as

$$SI = \log \frac{IAP}{K_{eq}},$$

where IAP is the ion activity product and K_{eq} is the equilibrium constant. Equilibrium is indicated when $SI = 0$, the water is supersaturated when $SI > 0$. If $SI < 0$, the water is undersaturated.

5.2 Inverse geochemical modelling

Inverse modelling calculates the transfer of moles (minerals/gases) that tend to dissolve or precipitate, and it also explains the chemical changes between the known initial and final solutions with respect to the available mineral phases. This is essential in understanding the causes for the transformation of chemical composition within the groundwater and surface water. To evaluate the geochemical evolution and chemical reactions along the flow direction, inverse modelling was carried out using PHREEQC. Mass balance calculation along a specific flow path was performed in the inverse modelling. During this inverse geochemical modelling, it was assumed that (i) the initial and final solutions represent the flows along the same flow direction, (ii) dispersion/diffusion do not affect the chemistry of water, and (iii) the mineral phases used in the model are exactly present in the aquifer. The modelling was carried out with the measured chemical composition of waters and the initial and final waters were L1–G1, G1–G2 and G2–L2 for all the sampling periods. That is the chemical composition of the surface water (L1/L2) and groundwater (G1/G2) represents the initial and final solutions for inverse geochemical modelling. The mineral phases that are likely to be present between these locations were also considered. Mineral phases included in the inverse modelling are obtained from the field observation and the geochemical studies were carried out in and around this region by Chaki *et al.* (2005) and Patnaik *et al.* (2016). The simulations were constrained within the pre-defined uncertainty limit of 0.05 (5%) or 0.1 (10%) as default for all the periods. By keeping the mineral phases constant, the inverse geochemical

Table 1. Hydrogeochemistry of surface water and groundwater.

Parameter	Unit	Mean		Range	
		Surface water	Groundwater	Surface water	Groundwater
pH	pH scale	–	–	7.2–9.3	6.8–7.9
EC	$\mu\text{S}/\text{cm}$	1005	1444	617–1674	1189–1909
Calcium	mg/l	52	59	40–82	42–75
Magnesium	mg/l	22	34	19–30	10–75
Sodium	mg/l	95	141	50–143	66–255
Potassium	mg/l	5	7	1–7	1–18
Bicarbonate	mg/l	235	351	175–341	263–488
Chloride	mg/l	113	175	65–164	112–275
Sulphate	mg/l	42	76	25–64	53–106
Nitrate	mg/l	48	43	21–80	28–66
Uranium	$\mu\text{g}/\text{l}$	12	27	2–33	13–52

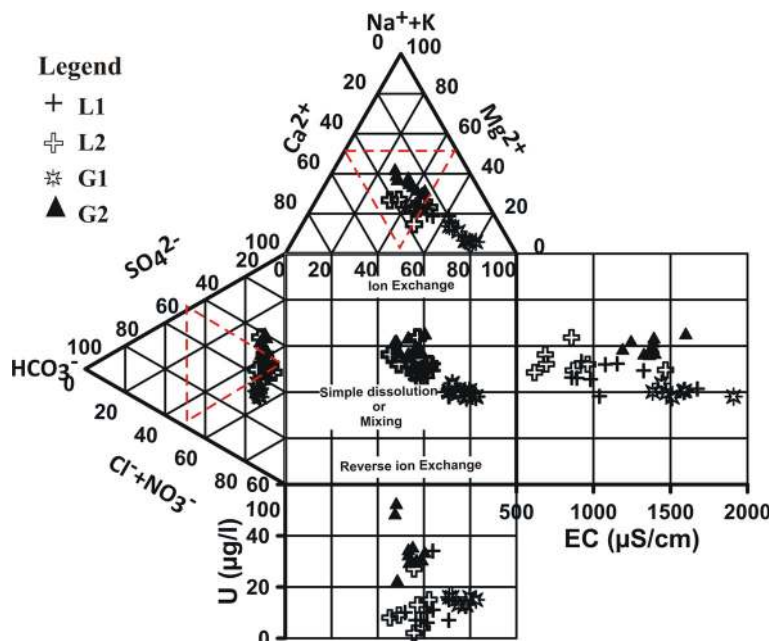


Figure 3. Hydrogeochemical facies of surface water and groundwater (Durov 1948).

modelling was carried out for all sampling periods to understand the temporal changes in the surface and groundwater interaction.

6. Results and discussion

6.1 Chemical characterisation of surface water and groundwater

The mean and range of pH, EC, calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulphate and nitrate concentration in the surface water and groundwater samples collected around the uranium mineralised zone are given

in table 1. The dissolved solids are comparatively high in groundwater than the surface water as indicated by EC. The concentration of nitrate alone is slightly higher in surface water, whereas rest of the major ions in groundwater is higher than surface water. Since this region is intensively cultivated and the runoff discharges into the lakes, high concentration of nitrate (Bureau of Indian Standards permissible limit 45 mg/l) was observed in both the surface water (53% of samples) and groundwater (41% of samples). Hydrochemical facies identified by a double triangular plot (Durov 1948) (figure 3) indicates that the surface water (L1 and L2) and groundwater (G2) fall in the mixed Ca–Mg–Cl type, whereas groundwater from the

Table 2. Percentage range of U speciation in surface water and ground-water.

L. no.	Nature of water	Speciation form	Percentage range
L1	Lake (upstream)	$UO_2(CO_3)_3^{4-}$	21–91
		$UO_2(CO_3)_2^{2-}$	9–77
		$UO_2(CO_3)$	0–2
L2	Lake (downstream)	$UO_2(CO_3)_3^{4-}$	9–76
		$UO_2(CO_3)_2^{2-}$	24–85
		$UO_2(CO_3)$	0–6
G1	Groundwater (upstream)	$UO_2(CO_3)_3^{4-}$	31–64
		$UO_2(CO_3)_2^{2-}$	36–68
		$UO_2(CO_3)$	0–1
G2	Groundwater (downstream)	$UO_2(CO_3)_3^{4-}$	17–54
		$UO_2(CO_3)_2^{2-}$	46–80
		$UO_2(CO_3)$	0–3

G1 well was of Na–Cl type. It indicates that the hydrogeochemistry of groundwater flow from the upstream region is transformed from Na–Cl type to the mixed Ca–Mg–Cl type when it enters into the mineralised zone of the downstream region due to the presence of carbonate rocks and the continuous infiltration of surface water (L1).

Uranium concentration during all the sampling campaign ranges from 2 to 52 µg/l. The mean and range of uranium concentration in surface water and groundwater are given in table 1. The concentration of uranium is higher in groundwater when compared to surface water in most of the sampling campaigns (figure 3). The uranium concentration increases along the flow path (L1–G1–G2) and decreases in L2 (when compared with G2). An inconsistent range of uranium concentration was observed throughout the sampling campaign between flow path G2–L2, which is due to the sudden variation of pH, Eh, temperature and exposure to surface water (L2), resulting in instability of uranium complex in water.

6.2 Geochemical speciation

The mobility of uranium in water is controlled by uranium speciation; hence, it is important to know the dominant uranium species in order to predict its migration and distribution. Factors controlling the uranium speciation are pH, Eh, concentration of ions/ionic strength and the different mineral phases during the interaction process (Bernhard *et al.* 1996). Based on PHREEQC output, the uranium tetravalent ion complex exists in various forms of species such as $U(OH)^{5-}$, $U(OH)^4$, U^{4+}

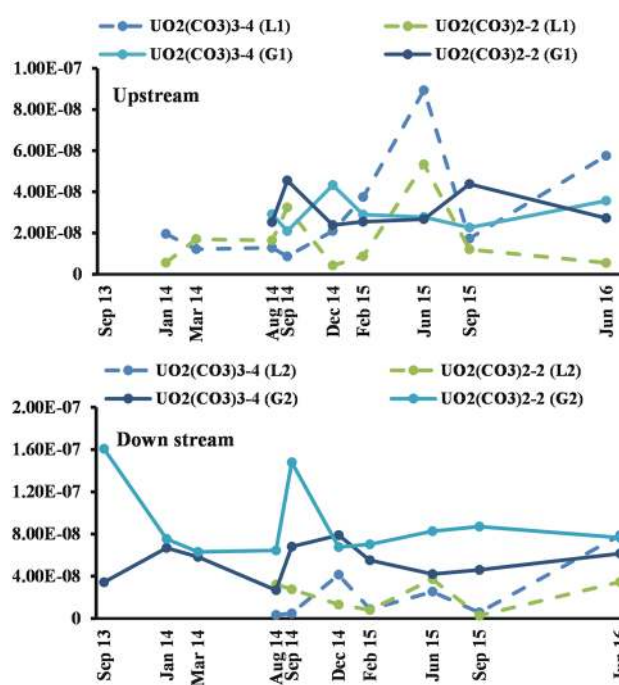


Figure 4. Temporal variation of U species in surface water and groundwater of upstream and downstream regions around the mineralised zone.

and uranium hexavalent complex exhibits in the form of $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)$, UO_2OH^+ , UO_2^{2+} , $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)^{5+}$. Species calculation displays that the uranium complexes of $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ are common in aqueous solution, whereas the complexing of the types such as $U(OH)^{5-}$, $U(OH)^4$, U^{4+} , $UO_2(CO_3)$, UO_2OH^+ , UO_2^{2+} , $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)^{5+}$ were minimal in surface and groundwater of this region. Formation of uranyl carbonate complexes $UO_2(CO_3)_3^{4-}$ and UO_2

(CO₃)₂⁻ is favourable because of neutral to alkaline pH (Hsi and Langmuir 1985; Pabalan *et al.* 1996; Nair and Merkel 2011) of water and the weathering of carbonate rocks present in this region. Table 2 shows the percentage range of uranium species distributions in the lake and groundwater present in the upstream and downstream regions. Temporal variation of uranium species is shown in figure 4, and it indicates that the groundwater of downstream region is abundant with uranium species due to increase in the release of uranium from the

mineralised zone at deeper depth along the slope direction.

6.3 Validation of interaction based on water level fluctuations

The groundwater level in this region ranges between 1 and 5 m below the ground level. L1 lake contains water throughout the year, whereas L2 lake contains water during monsoon and post-monsoon and is almost dry during summer. Discharge of surface water from upstream to downstream (L1–L2) was observed in the field during monsoon where the movement of water was clearly visualised. Based on the measured surface water and groundwater levels, the spatial and temporal variation was prepared (figure 5). Spatial and temporal variations of surface water and groundwater levels indicate that the rainfall plays a major role, which controls the recharge and discharge of this region. It also reveals that the direct runoff from the L1 lake (upstream) to the L2 lake (downstream) took place during high rainfall periods. Both the lakes were filled quickly in the beginning of monsoon itself due to increase in rainfall recharge and excess runoff from surrounding areas. During the onset of monsoon, the water level in the lakes L1 and L2 rises and the water seeps into G1 and G2, respectively. The water from the G1 further flows into G2. The groundwater level gradually rises during the monsoon to a depth less than 1 m from the surface. During the post-monsoon, L1 seeps into shallow groundwater (G1) from which the water flows into G2. The groundwater (G2) further flows into lake L2 due to the difference in water levels. It shows that recharge from lakes to groundwater and groundwater to lakes varies during pre-monsoon/monsoon and post-monsoon, respectively.

6.4 Validation of interaction based on SI

Hydrogeochemistry of surface water and groundwater is used as an input to represent the extent to which the water is chemically in equilibrium

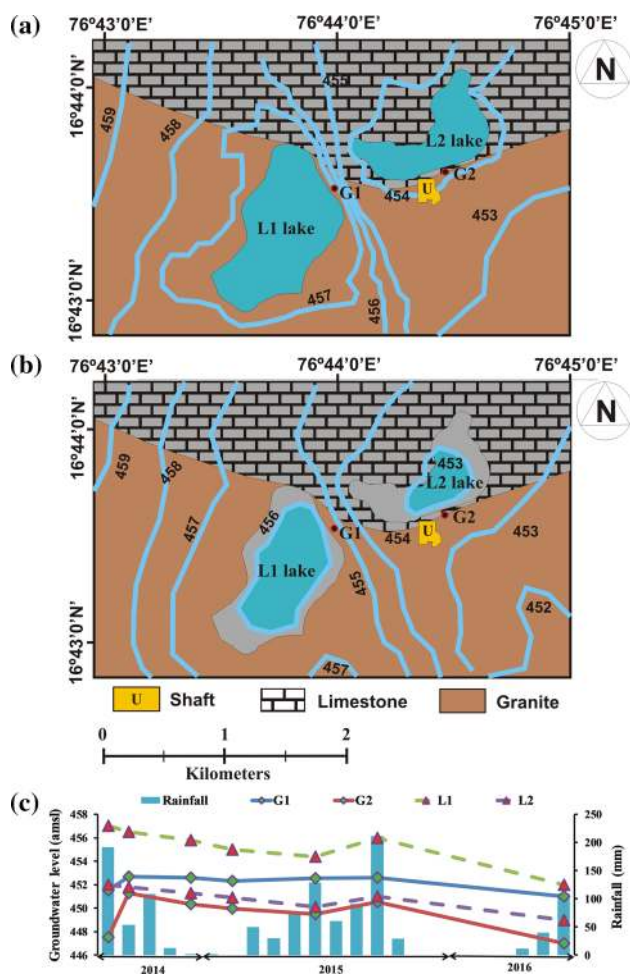


Figure 5. Spatial variation of groundwater level during (a) monsoon, (b) non-monsoon, and (c) temporal variation of surface water and groundwater levels (m amsl).

Table 3. Minimum and maximum of calculated mineral SI.

Phase	Composition	Minimum		Maximum	
		Lake	Groundwater	Lake	Groundwater
Calcite	CaCO ₃	-0.26	-0.27	1.31	0.47
Dolomite	CaMg(CO ₃) ₂	-0.57	-0.52	2.61	0.9

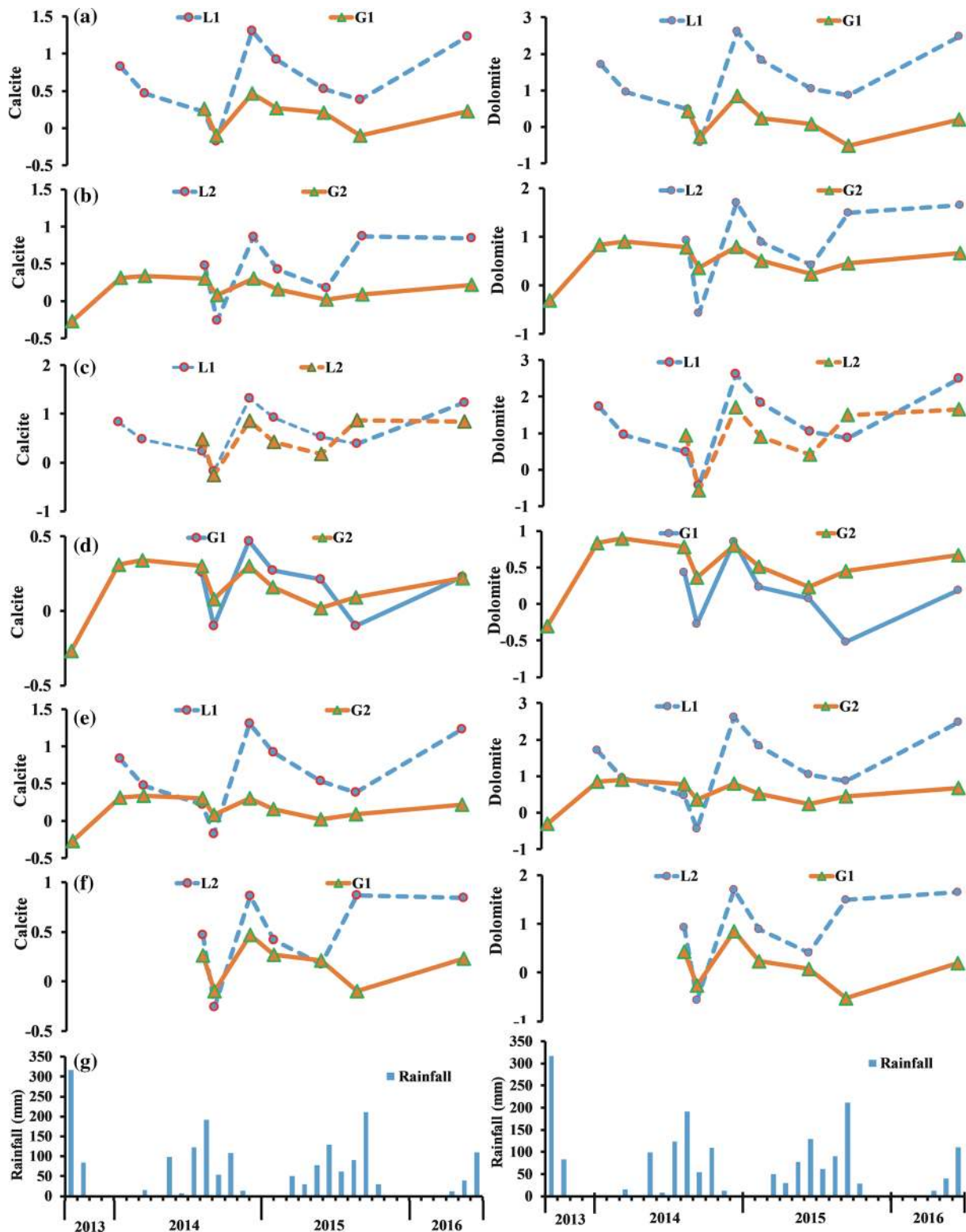


Figure 6. Comparison between the temporal variation of the SI with respect to rainfall: (a) L1 lake–G1 well, (b) L2 lake–G2 well, (c) L1 lake–L2 lake, (d) G1 well–G2 well, (e) L1 lake–G2 well, (f) L2 lake–G1 well and (g) temporal variation of rainfall.

with respect to the minerals present in the aquifer system. Mineral phases such as calcite and dolomite were considered owing to the presence of carbonate minerals in limestone rock. Table 3 shows the

minimum and maximum mineral SIs observed from the PHREEQC.

Temporal variation of SI was prepared to understand the interaction process and is compared with

the rainfall data, which is a major controlling factor for mineral saturation level. The carbonate minerals such as calcite and dolomite show an increasing trend during monsoon due to the dissolution of limestone rock. Comparison between the mineral SI of lake water and groundwater collected during several periods of sampling was plotted to understand the effects of lake water over groundwater and *vice versa*. In this study, six different comparisons were interpreted to understand the interaction process which include (i) L1 lake–G1 well, (ii) L2 lake–G2 well, (iii) L1 lake–L2 lake, (iv) G1 well–G2 well, (v) L1 lake–G2 well and (vi) L2 lake–G1 well.

Comparison between upstream region (L1–G1) and downstream region (L2–G2) reveals that a

higher degree of interaction was observed in the downstream region (figure 6a and b). In downstream region (L2–G2), the influence of lake water over groundwater is dominant during the monsoon due to rainfall recharge. Figure 6(c and d) indicates that lake water (L1–L2) and groundwater (G1–G2) express a similar pattern in the SI value indicating a strong correlation that depicts the common source of origin. Cross-comparison of lake water and groundwater (L1–G2 and L2–G1) (figure 6e and f) expresses a strong correlation during the monsoon and less in post-monsoon. This indicates that recharge from L2, which was dominant in monsoon, will inverse during summer (i.e., groundwater in the upstream region recharge the L2 during the dry season).

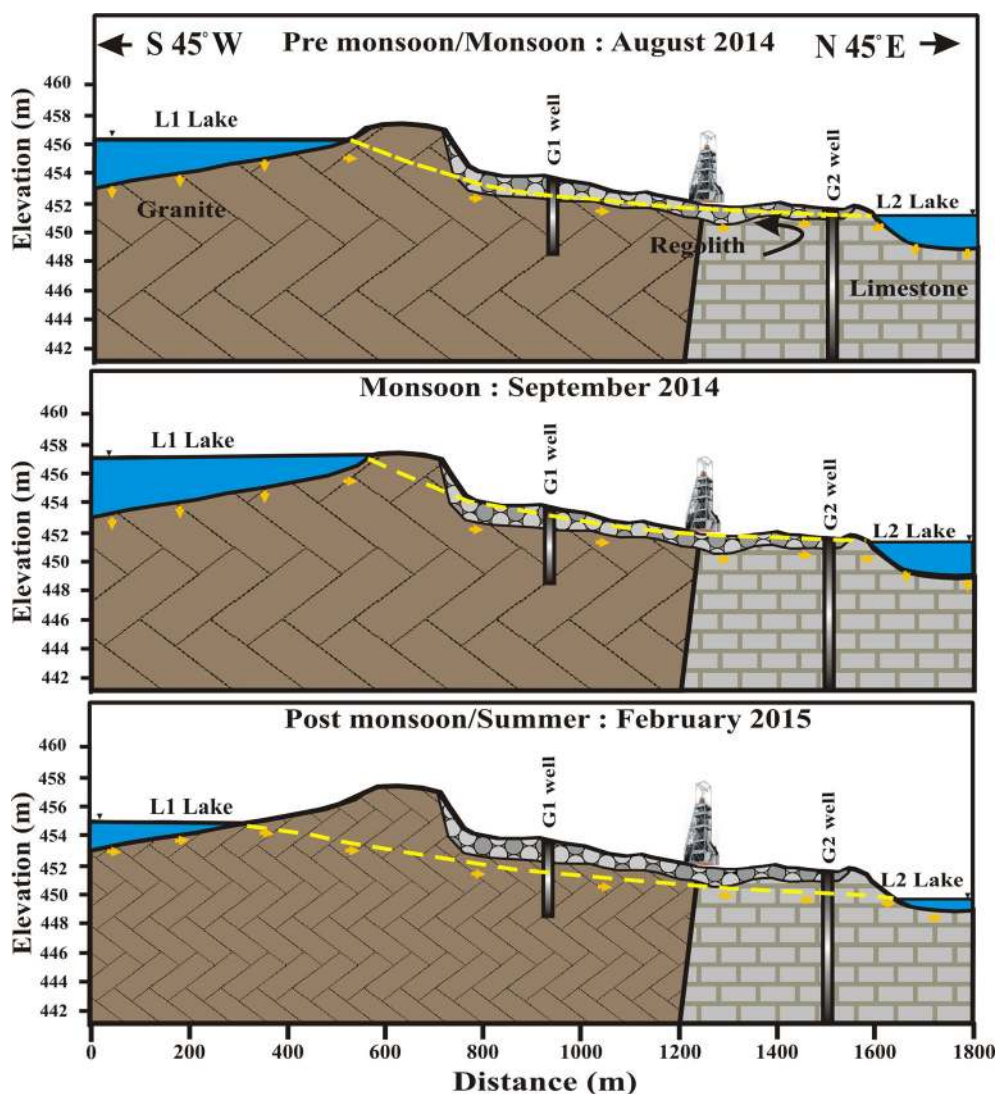


Figure 7. Schematic view of surface water and groundwater interaction near the uranium mineralised zone.

6.5 An idealised interaction process based on SI value

Based on the comparison between the SI values of lake water (L1–L2) and its adjacent groundwater (G1–G2), the following interpretations are made:

- (i) The SI value of L2 and G2 in the downstream region follows similar pattern due to same source and continuous recharge from the lake L1.
- (ii) Degree of interaction between the lake (L2) and the groundwater (G2) is higher in the beginning of monsoon due to the recharge from L2, which occurs only during the onset of monsoon.
- (iii) A similar trend of SI value was observed in groundwater of upstream (G1) and downstream (G2) indicating that the groundwater (G2) has evolved from G1.
- (iv) Interaction between G1–G2 and L2 is higher during summer, which indicates that L2 is recharged from groundwater (G2) which is recharged by G1.

With the above results, various schematic diagrams were prepared to understand the interaction between surface water and groundwater near the uranium mineralised region (figure 7).

6.6 Hydrogeochemical evolution by inverse modelling

Inverse modelling was performed with three simulations (L1–G1, G1–G2 and G2–L2) (figure 8) along the same flow path with the primary mineral phases including aragonite, biotite, calcite, chlorite, coffinite, dolomite, gypsum, halite, K-feldspar, plagioclase, quartz and uraninite which are reported by Chaki *et al.* (2005) and Patnaik *et al.* (2016) for this study region. Analytical values (major ions and uranium) of the water samples for each period were used to represent the initial and final solutions along the flow direction. Figure 8 shows the suitable model which has been selected based on the criteria of ‘the sum of residuals and maximum fractional error’ from all the models generated by PHREEQC. It represents

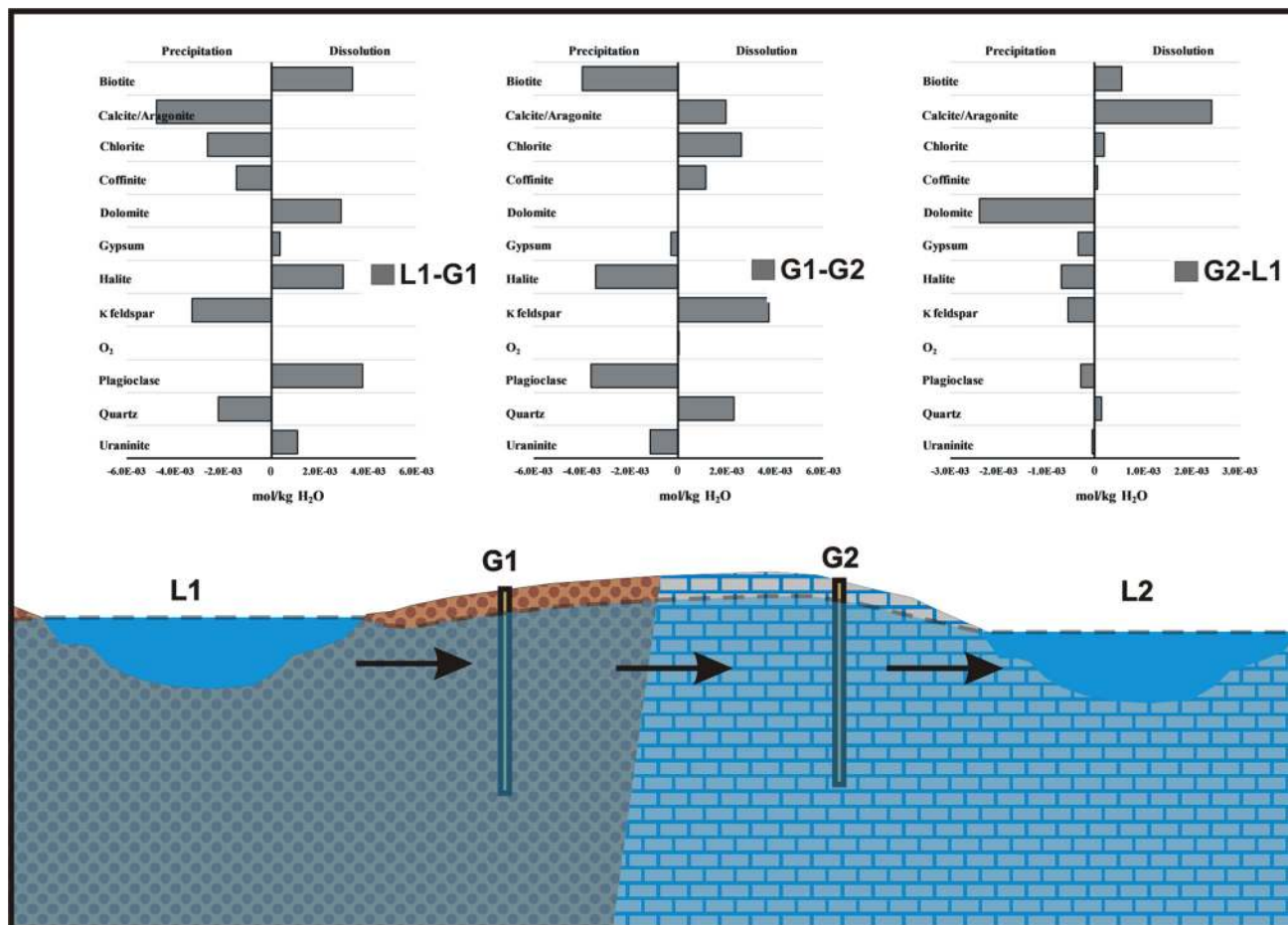


Figure 8. Hydrogeochemical evolution/phase mole transfer along the flow line.

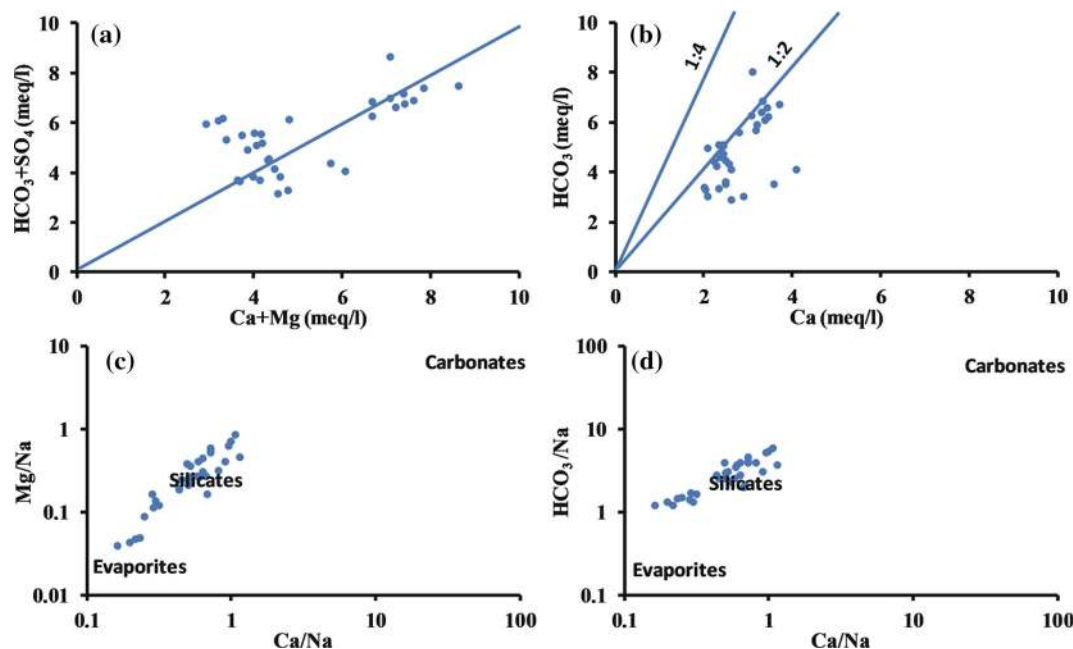


Figure 9. Bivariate plots indicating weathering trends: (a) $\text{Ca}+\text{Mg}$ vs. HCO_3+SO_4 , (b) Ca vs. HCO_3 , (c) Ca/Na vs. Mg/Na and (d) Ca/Na vs. HCO_3/Na .

most possible combinations of reactants and products that are responsible for the hydrogeochemical evolution. In upstream region (L1–G1), precipitation of aragonite, calcite, quartz, K-feldspar and chlorite indicates the dominance of silicate weathering and carbonate weathering (figure 8). Since G1 is located in the agricultural land, the precipitation of gypsum and halite was observed along the flow path of G1–G2, which is derived from the irrigation return flow that is concentrated with the ions such as sodium and sulphate which are present in fertilisers and calcium from the soils that are derived from the adjacent carbonate rocks. From G2 to L2, the precipitation of carbonates, plagioclase, coffinite, gypsum and halite indicates the combined process of weathering and dissolution of evaporites computed by the inverse modelling which is also confirmed by the bivariate plot (figure 9). Figure 9(a) indicates that the points falling along the equiline may have originated from weathering of sulphate and carbonate minerals as suggested by Datta and Tyagi (1996). Figure 9(b) suggests that the points falling along 1:2 line have resulted from weathering of calcite (Mackenzie and Garrels 1971; Holland 1978). Figure 9(c and d) suggests that both silicate and evaporites are responsible for the changes in hydrogeochemistry of both the surface water and groundwater. The present study region is highly complex with respect to geology; the reactions that are

responsible for the changes in hydrogeochemistry of water do not result from a single source, but from multiple sources which are depicted in figure 9. Since the precipitation and dissolution kinetics of silicate minerals are slow, the moles released from these minerals are very less.

7. Conclusions

Hydrogeochemical modelling was used to understand the interaction between surface water and groundwater in a uranium mineralised region. Hydrogeochemically, surface water and groundwater were mainly of mixed Ca–Mg–Cl type except in the groundwater of upstream region which is of Na–Cl type. Uranium species in surface water and groundwater was dominated by $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ hexavalent complexes. The lake on the western side always contributes to groundwater recharge, whereas during most part of the year groundwater is discharged to the lake on the eastern side. The rainfall results into change in the geochemical nature of water in the lake by way of changing the saturation indices from oversaturated to undersaturated level. The precipitation and dissolution of carbonate minerals were the major reactions that are responsible for the changes in the hydrogeochemistry in comparison with silicate minerals. Hence, carbonate

weathering, silicate weathering and irrigation return flow are the dominant processes that govern the hydrogeochemical evolution in this region during the interaction process. Thus, the geochemical modelling helped to understand the temporal changes in the interaction between surface water and the groundwater in a uranium mineralised region which cannot be estimated by simple water level measurements.

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