Geochemical characterization of surface water and spring water in SE Kashmir Valley, western Himalaya: Implications to water–rock interaction

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Water samples from precipitation, glacier melt, snow melt, glacial lake, streams and karst springs were collected across SE of Kashmir Valley, to understand the hydrogeochemical processes governing the evolution of the water in a natural and non-industrial area of western Himalayas. The time series data on solute chemistry suggest that the hydrochemical processes controlling the chemistry of spring waters is more complex than the surface water. This is attributed to more time available for infiltrating water to interact with the diverse host lithology. Total dissolved solids (TDS), in general, increases with decrease in altitude. However, high TDS of some streams at higher altitudes and low TDS of some springs at lower altitudes indicated contribution of high TDS waters from glacial lakes and low TDS waters from streams, respectively. The results show that some karst springs are recharged by surface water; Achabalnag by the Bringi stream and Andernag and Martandnag by the Liddar stream. Calcite dissolution, dedolomitization and silicate weathering were found to be the main processes controlling the chemistry of the spring waters and calcite dissolution as the dominant process in controlling the chemistry of the surface waters. The spring waters were undersaturated with respect to calcite and dolomite in most of the seasons except in November, which is attributed to the replenishment of the CO₂ by recharging waters during most of the seasons.

1. Introduction

The karst landscape is characterized by the outcropping of soluble rocks (limestone, dolomite, gypsum) that exhibit unique surface and sub-surface landforms and distinct hydrology (White 1988; Ford and Williams 2007). Karst aquifers are characterized by an underground drainage system including fractures, dissolution generated conduits and caves that permit the transport of water (Milanovic 2001). The well connected channel system and well observed cave system in the karst

environment is the subsurface equivalent of dendritic river system (Palmer 1991). Karst areas are considered to be a vulnerable habitat for highly diversified vegetal and animal species (Juberthie and Decu 1994; Christman and Culver 2001) and the sediments and speleothems in caves have paleontological (Latham *et al* 2007) and paleoclimate significance (White 2004, 2007; Sasowsky 2007). Due to a number of geological, morphological and hydrological features, karst areas are particularly prone to environmental degradation and irreversible landscape damages caused by the

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negative impact of human activities (White 1988; Gams *et al* 1993; Williams 1993; Nicod *et al* 1997; Akdim and Amyay 1999; Burri *et al* 1999; Urich 2002; Parise and Pascali 2003; Bonaccio 2004; Calò and Parise 2006; Sauro 2006; Parise and Gunn 2007). Urbanisation, stone clearing, deforestation and uncontrolled quarrying in catchment areas have transformed, disturbed and partially or totally destroyed the karst landscape causing modification of the surface and underground drainage, and deterioration in the quality of groundwater (Sauro 1993; Smith 1993; Frumkin 1999; Ginés 1999; Kacaroglu 1999; De Waele and Follesa 2004; Spizzico *et al* 2005; Delle Rose *et al* 2007; Gunn 2007).

The carbonate rocks cover about 20% of the world's continents (Ford and Williams 2007) and as an aquifer it is the most productive source of

groundwater in the world. Carbonate aquifers represent the principal reservoir of freshwater in south-eastern (Anantnag), southwestern (Pulwama) and western Kashmir (Budgam), where most of the public-supply water is derived from the carbonate aquifer. In southeast Kashmir the karst features are not visible in large scale. Karren fields, a few caves (cross section of 1 to 3 m) and a few conduits (cross section of a few cm) are exposed near some springs, recharge areas and limestone quarry sites. The exposed karst features and the anomalously high discharge of the springs (up to 2000 L s^{-1}) with tremendous fluctuations is a good indication of a well developed karst system.

Surface water and groundwater chemistry provide important information on the sources of dissolved loads, chemical weathering and chemical characteristics of a drainage basin and subsurface

Figure 1. Location of the study area and the sampling sites across SE Kashmir Valley. The details of sampling IDs used in the map are given in table 1 with numbers 1, 2, 3, ... for springs and S1, S2, S3, ... for streams.

lithology (Drever 1988; Négrel *et al* 1993; Han and Liu 2004; Hunkeler and Mudry 2007 and others). Numerous studies have been carried out to examine the source rocks affecting the chemical composition of natural waters (Potter 1978; Sarin *et al* 1989; Edmunds and Smedley 2000; Karim and Veizer 2000; Quade *et al* 2003; Singh *et al* 2005 and others). These studies have shown that chemical weathering of rocks in a drainage basin is largely controlled by carbonate dissolution. Despite the societal importance of these streams and springs, only little is presently available on the chemical composition of these pristine waters (Jeelani 2005).

In this study, extensive analyses of surface and spring waters of SE Kashmir Valley have been carried out to determine the geochemical processes controlling the water chemistry in a non-industrial and less human affected area of western Himalaya.

2. Study area

Kashmir Valley in the western Himalaya has rich water resources in the form of streams, lakes, springs and groundwater. In the SE Kashmir Valley, numerous springs are emanating from Triassic Limestone, Permo-Carboniferous Panjal Traps, Quaternary Karewas and Recent Alluvium (Jeelani 2005). The study area is located in the southeastern part of the Kashmir Valley in the northern part of India (figure 1). The area lies between the latitudes 33°20'N and 33°15'N and longitudes 74°30'E and 75°35'E, covers an area of about 3984 km². The area experiences well defined four seasons (spring, summer, autumn and winter) and the climate is humid and temperate. Mean annual precipitation is 1100 mm, mainly falling during winter and spring. Mean monthly air temperature ranges from -15°C in January to 37°C in July. The most economic activity of the area is agriculture and horticulture, and the farm land is mainly planted with paddy, mustard, apple, plum, peach, etc.

Kashmir Valley is characterized by a diverse geological record ranging in age from Pre-Cambrian to Recent (Middlemiss 1910, 1911; Wadia 1975; GSI 1977). The geology of Anantnag is dominated by the Upper Paleozoic and Triassic rocks (figure 2). The Triassic rocks are surrounded by Palaeozoics and are overlain by Pleistocene and Recent sediments. Upper Palaeozoic rocks (Agglomeratic Slates and Panjal Traps) occur towards the marginal areas. The lithology of Upper Palaeozoics include andesitic/basaltic lavas, pyroclastics and arenites. The Palaeozoic rocks are overlain by Triassic Limestone, which consists mostly of a thick series (~1000 m) of compact blue limestone, argillaceous limestone and dolomitic limestone

(Middlemiss 1910) and occur in the form of dissected ridges. The limestone is mostly thin bedded, with common shale and sandstone horizons. The fluvio-glacial and fluvio-lacustrine deposits of Pleistocene are locally known as Karewas, which consist of fine lacustrine sandstones, beds of loess, conglomerates, etc. Karewas at many places stand >100 m above the alluvial plain and form plateau like features. Small valleys between Triassic Limestone ridges and Karewas are filled with Recent Alluvium, which consists of fine muddy and silty sediments. However, along the streams the boulders and gravels predominate.

Triassic Limestone is the most significant and main aquifer of south Kashmir which supplies water to more than one million people of Anantnag for domestic and agriculture purposes (Jeelani 2007). The underlying Palaeozoic rocks are mostly impermeable (Coward *et al* 1972). The overlying Karewas are not productive aquifers (Jeelani 2007)

Figure 2. Geological map of the study area.

but act as efficient filters owing to their high porosity. Due to the low hydraulic conductivity, alluvium blocks the water flowing through the Triassic Limestone (Jeelani 2008) and the water emerges out in the form of springs at the contact between the alluvium and Triassic Limestone.

3. Analytical techniques

Water samples were collected from precipitation, snow melt, glacial melt, streams and springs across the SE Kashmir Valley during November 2007, March 2008, May 2008 and July 2008 (figure 1).

Table 1. *Sampling details of surface and subsurface water samples of SE part of Kashmir Valley.*

Sampling code	Location	Sample type	Latitude			Longitude			Elevation m
			Deg	Min	Sec	Deg	Min	Sec	
Ppt-1	Anantnag	Precipitation	33	43	866	75	91	223	1616
Ppt-2	Kolahai	Precipitation	34	12	657	75	17	767	3221
GL-1	Shesnag	Glacial lake	34	05	656	75	29	496	3594
GL-2	Tarsar	Glacial lake	34	08	628	75	8	232	3620
GM-1	Kolahai	Glacial melt	34	11	628	75	20	232	3477
SM-1	Chandanwari	Snow melt	34	04	613	75	24	699	2898
SM-2	Aru	Snow melt	34	05	302	75	15	838	2435
SM-3	Satlangen	Snow melt	34	11	866	75	16	331	3044
STR-1	West Liddar 1	Stream	34	09	424	75	14	486	2787
STR-2	Tarsar	Stream	34	09	424	75	14	486	2787
STR-3	West Liddar 2	Stream	34	05	302	75	15	838	2425
STR-4	Katernag	Stream	34	05	302	75	15	838	2425
STR-5	East Liddar 1	Stream	34	04	333	75	22	933	2362
STR-6	Athir	Stream	34	04	333	75	22	933	2362
STR-7	East Liddar 2	Stream	34	00	957	75	18	532	2080
STR-8	West Liddar 3	Stream	34	01	513	75	18	617	2151
STR-9	Liddar 1	Stream	33	57	506	75	18	380	2020
STR-10	Langi Nallah	Stream	33	57	506	75	18	380	2020
STR-11	Kuthar	Stream	33	47	388	75	22	601	2169
STR-12	Bringi	Stream	33	36	195	75	17	654	2110
STR-13	Sandran	Stream	33	27	560	75	22	252	2126
STR-14	Liddar 2	Stream	33	45	707	75	07	684	1593
STR-15	Jhelum River	Stream	33	45	707	75	07	684	1593
SPR-1	Andernag	Spring	33	43	866	75	91	223	1616
SPR-2	Malakhnag	Spring	33	43	746	75	09	265	1618
SPR-3	Gajmag	Spring	33	44	027	75	09	735	1620
SPR-4	Hemalnag	Spring	33	44	027	75	09	735	1622
SPR-5	Gautamnag	Spring	33	44	362	75	10	979	1540
SPR-6	Martandnag	Spring	33	45	710	75	12	663	1641
SPR-7	Ayunnag	Spring	33	51	888	75	18	004	1989
SPR-8	Mamleshwarnag	Spring	34	00	587	75	18	712	2172
SPR-9	Manzgamnag	Spring	33	50	276	75	16	680	1794
SPR-10	Hapathnarnag	Spring	33	49	770	75	18	903	1885
SPR-11	Brarnag	Spring	33	48	480	75	17	395	1835
SPR-12	Kwarigamnag	Spring	33	43	779	75	15	922	1651
SPR-13	Shakarnag	Spring	33	42	547	75	18	942	1776
SPR-14	Daidnag	Spring	35	42	313	75	17	429	1730
SPR-15	Achabalnag	Spring	33	40	131	75	13	255	1656
SPR-16	Kongamnag	Spring	33	37	187	75	18	414	1922
SPR-17	Kokernag	Spring	33	35	208	75	17	791	1890
SPR-18	Lukhbawannag	Spring	33	40	566	75	10	117	1730
SPR-19	Kulamchinarnag	Spring	33	37	126	75	10	726	1717
SPR-20	Verinag	Spring	33	32	081	75	14	917	1880
SPR-21	Vetastanag	Spring	33	35	292	75	17	661	1814
SPR-22	Panzathnag	Spring	33	36	481	75	09	824	1728

Table 2. Summarized physico-chemical analytical results of stream and spring water samples of the study area.

Sample type	Sampling date & no.	Statistics	Temp. (°C)	pH	EC (µS/cm)	TDS (mg/l)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻ (µm/l)	SO ₄ ²⁻	Cl ⁻	SiO ₂	Ca/Mg
Precipitation	May/July 2008, N = 2	Min	10.2	8.6	64	64	104.8	40	8.7	0.3	262.2	20.8	6.8	23	2.6
		Max	11.8	8.9	78	78	140	40	34.8	0.5	295	47.9	35	28.8	3.5
		Mean	11	8.75	71	71	122.4	40	21.7	0.4	278.6	34.4	20.9	25.9	3.1
Glacial lake	July/November 2008, N = 3	SD	1.13	0.21	9.9	10	24.9	0	18.5	0.2	23.2	19.1	19.9	4.1	0.6
		Min	8	8.5	136	136	339.8	20	26.1	0.3	737.5	47.9	14.1	3.8	3.4
		Max	11	10.03	265	265	865.3	120	182.7	0.5	1802.8	70.8	105.5	15	43.3
		Mean	9.4	9.29	191.2	191	571.9	76	90.5	0.4	1212.8	61	54.8	8.4	19.4
		SD	1.53	0.77	69.86	70	277.3	52.9	88	0.1	557.8	12.4	47.9	6.3	22.9
Glacial melt	July/November 2008, N = 2	Min	3.8	9.8	40	40	72.4	20	0	0.3	65.6	56.2	20.9	22.6	3.6
		Max	5	12.2	60	60	84.8	20	43.5	2.6	81.9	77	28.2	26.3	4.2
		Mean	4.4	11	50	50	78.6	20	21.7	1.4	73.8	66.6	24.5	24.4	3.9
		SD	0.85	1.7	14.14	14	8.8	0	30.8	1.6	11.6	14.7	5.2	2.6	0.4
		Min	0.4	9	38	38	59.9	20	0	0.3	65.6	37.5	6.8	17.5	1.3
Snow melt	April 2008, N = 3	Max	8	9.5	154	154	309.9	240	43.5	1.3	655.6	210.3	91.7	21.6	5.2
		Mean	3.96	9.21	88	88	168.9	108	19.1	0.7	321.2	112.8	43.4	19.5	3.2
		SD	3.86	0.28	62.43	62	133.3	127	23	0.6	316.1	92.1	45.6	2.1	2
		Min	9	7.9	80	51	144.7	20	34.8	0.3	262.2	93.7	34.1	12	3.6
		Max	14	10.18	226	145	708.6	60	95.7	0.3	1311.1	185.3	112.8	25.3	16
Streams	November 2007, N = 4	Mean	11.25	8.94	149.67	96	417.5	43.3	71	0.3	729.3	125.6	83	19.4	9.8
		SD	2.32	1.08	62.76	40	239.8	19.1	27	0	450.9	44.5	37.2	6	5.3
		Min	2.2	7.5	110	70	249.5	60	0	0	655.6	0	77.6	12.8	1.9
		Max	14.2	8.2	230	147	648.7	200	548.1	0.5	1229.2	293.6	204.5	43.3	8.1
		Mean	6.02	7.81	167.91	107	426.3	120	164	0.2	878.0	111.4	134	27.7	4.1
	March 2008, N = 12	SD	3.87	0.21	45.36	29	126.8	43.9	161.3	0.2	196.0	83.9	40	9	1.9
		Min	3.3	7.7	56.5	36	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
		Max	18	8.4	291	186	18	18	18	18	18.0	18	18	18	18
		Mean	7.78	8.01	158.94	102	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
		SD	4.23	0.2	64.63	41	186.6	67.8	57.4	0.5	336.5	102.4	17	6.7	107
	July 2008, N = 15	Min	5.7	7	96	61	104.8	20	26.1	0.3	229.4	29.1	6.8	4.5	1.3
		Max	19.4	12.8	307	196	911.2	160	252.3	3.1	1966.7	320.6	70.5	23.3	9
		Mean	12.37	8.42	162.82	104	408.1	101.2	81.4	1	812.7	148.1	17.3	13.4	4.4
		SD	3.93	1.42	60.49	39	237.2	47.7	56.1	0.7	467.4	84.3	16.6	5.4	2.2

Table 2. (Continued).

Sample type	Sampling date & no.	Statistics	Temp. (°C)	pH	EC (µS/cm)	TDS (mg/l)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻ (µm/l)	SO ₄ ²⁻	Cl ⁻	SiO ₂	Ca/Mg
Springs	November 2007, N = 13	Min	11	8	186	119	179.6	120	104.4	0	737.5	79.1	49.1	5.5	0.5
		Max	22	9.11	470	301	1163.2	559.9	1513.7	1.5	2950.1	283.2	218	53.3	5.9
		Mean	15.07	8.68	360	230	732.7	350.6	555.7	0.5	2147.0	177.1	122.8	19.1	2.6
		SD	3.24	0.34	89.54	57	270.1	137.2	427.1	0.4	654.8	57.5	48.1	12.7	1.6
	March 2008, N = 19	Min	8.3	6.1	160	102	352.3	80	87	0	983.4	29.1	21.2	12.3	0.4
		Max	20.6	7.7	532	340	1235	1039.8	1513.7	3.1	3671.2	220.7	430.1	35.9	6.9
		Mean	13.3	7.07	354.90	227	764	370.3	582	0.6	2261.7	114.6	201.5	22.9	3
		SD	3.37	0.39	109.51	70	284.3	235.2	419.8	0.7	815.3	54	109.2	6.3	1.7
	May 2008, N = 20	Min	8.9	6.4	142	91	159.9	160	95.7	1.3	737.5	12.5	56.4	5.8	0.4
		Max	21	8	624	399	1054.9	1459.7	1766	12.3	4507.0	329	352.6	27	4.8
		Mean	13.65	7.32	331.52	212	565.6	456.1	577.5	3.9	2042.4	161.3	147.1	12	1.8
		SD	3.02	0.37	118.18	76	308.3	298.9	444.2	2.7	869.2	85.4	79.8	6.3	1.1
	July 2008, N = 22	Min	10.1	6.4	236	151	354.3	100	87	0.5	1147.2	37.5	6.8	4.7	0.4
		Max	21.2	8.5	510	326	1303.9	979.8	1687.7	9.7	3441.7	383.1	225.7	27	8.5
		Mean	14.43	7.35	392.21	251	859.7	424.9	500.2	2.8	2543.7	155.2	78.4	13.5	3.2
		SD	2.81	0.47	72.69	46.52	282.5	244.5	422.4	2.3	583.5	85.7	65.6	6.1	2.3

May and November represent peak and lean discharge, respectively, while March and July are the medium discharge period for streams and springs. The samples were filtered using 0.45 µm nylon membrane Millipore filters and separated in to two aliquots of 500 ml volume. One of the filtered aliquot was acidified with ultrapure HNO₃ for cations and trace elements and the other aliquot was preserved unacidified for anion measurements. In addition, one unfiltered sample (~250 ml) was also collected for alkalinity measurements. The standard methods were adopted to analyse the dissolved chemical constituents (APHA, AWWA, WEF 2001).

Temperature, pH, conductivity (EC) and alkalinity were measured at site. The major ion analysis was carried out at the Geochemistry Lab of Department of Geology and Geophysics, University of Kashmir, Srinagar. Alkalinity was measured by HCl titration; Ca²⁺ and Mg²⁺ by EDTA titration; Cl⁻ by AgNO₃ titration; SO₄²⁻ by spectrophotometry; Na⁺ and K⁺ by flame emission photometry. Ca²⁺, Mg²⁺, Na⁺ and K⁺ of some samples were also determined using ICP-MS for cross check and the correction was within ±5%. In most of the water samples, the total cation charge (TZ⁺ = Ca²⁺ + Mg²⁺ + Na⁺ + K⁺ in meqL⁻¹) balances that of the total anions (TZ⁻ = HCO₃⁻ + Cl⁻ + SO₄²⁻ in meqL⁻¹) within analytical uncertainties and the normalized inorganic charge balance (NICB = (TZ⁺ - TZ⁻)/TZ⁺ × 100%) is within ±5%.

4. Results and discussion

Sample details and physico-chemical characteristics of precipitation, snow melt, glacial melt, stream water and spring water are shown in tables 1 and 2. In the present investigation, Na has been corrected for contributions from precipitation and halite by assuming all Cl⁻ is contributed to streams and spring water from the precipitation and/or halite dissolution (Na* = Na - Cl) (Sarin *et al* 1989; Singh *et al* 1998; Krishnaswami *et al* 1999; Dalai *et al* 2002; Singh *et al* 2005).

4.1 Physical characteristics of spring and stream water

The data for temperature (*T*), pH and electrical conductivity of the karst spring waters and streams, collected in November 2007, March 2008, May 2008 and July 2008 are summarised in table 2. The spring waters are fresh, colourless, odourless and cold with lower *T* (range: 8.9°–15.5°C, mean: 12.9, standard deviation: 1.76). In addition, there are a few warm springs (Malakhnag, Gajmag, Hemalnag, Gotamnag) with temperatures close to

Figure 3. Temperature *vs.* altitude plot showing increase of temperature with decrease in altitude of the springs.

20°C. The water temperatures were found to be 0.1°C lesser before noon than in the evening. This may be attributed to the local warming of the immediate spring area after noon. There is a clear relationship between the altitude of the springs and the temperature of the spring waters. Temperature increases with the decrease in altitude (figure 3). Unlike the springs, the temperature of the streams corresponds to the ambient temperature and increases with increase in the distance from its source and with increase in time from morning to evening.

As expected, the surface and spring waters are alkaline with low to medium electrical conductivity. High EC of the springs is attributed to the more time for water to interact with the host rock.

4.2 Spatial and temporal variability in total dissolved solids

The total dissolved solids (TDS) in the stream water and spring water samples (table 2), of SE

Figure 5. Positive correlation of Achabalnag and Andernag with Bringi stream and Liddar stream, respectively.

Kashmir Valley vary from 36–196 mg L⁻¹ and 91–399 mg L⁻¹, respectively. In general, TDS shows an increase in concentration with decrease in altitude (figure 4). However, some stream water samples showed higher TDS values (figure 4) is attributed to their source from the high altitude lakes (Tarsar, Dodsar, Shishnag, etc.) with higher TDS values (table 2). Even some spring water samples have lower TDS at lower altitudes. This is an indication that these karst springs (Achabalnag, Andernag, Martandnag) are recharged by the nearby streams with the similar TDS values. Best correlation of the chemical parameters between Achabalnag and Bringi (figure 5) supports the above hypothesis and reflects that the spring is mainly recharged by the Bringi stream. The dip of carbonate rocks at a place known locally as Adigam, a sinking stream, also favours the recharge by the stream. Positive correlation of the solutes between Andernag spring and Liddar stream favours the recharge of the spring by the Liddar stream. The less defined correlation between the Martandnag and the nearby stream (Liddar) may be due to less contribution of recharge from the stream. However, lower TDS in Martandnag during May is attributed to dilution due to recharge by various streams/canals flowing

Figure 4. TDS *vs.* altitude plot of springs and streams.

Figure 6. Piper trilinear diagram showing possible water types.

Figure 7. $\text{Ca}/(\text{Ca} + \text{Mg})$ vs. $\text{SO}_4/(\text{SO}_4 + \text{HCO}_3)$ and Ca/Mg vs. Mg plots.

in the area during the period for paddy fields. The percolating water is filtered by the sedimentary rocks around the Martand hillock. Sinking streams is a common process in most of the karst areas of the world (Ford and Williams 2007). Kongamnag, one of the high altitude springs, owes its high TDS from the hosted unconsolidated Karewa sediments. TDS values of the warm springs was higher ($>250 \text{ mg L}^{-1}$) owing to their long subsurface circuitous route and interaction with diverse host lithology. The TDS of the stream and spring waters were low during the snow melting period (May) compared to the other months.

4.3 Major ion composition

The triangular diagrams for cations and anions (figure 6) show variations in chemical composition of surface water and spring waters, which is dominated by Ca^{2+} , Mg^{2+} and HCO_3^- . In surface water samples, Ca^{2+} is the dominant cation contributing $>50\%$ to the cation budget followed by Mg^{2+} ($<30\%$) and Na^+ ($<20\%$). In most of the spring water samples, Ca^{2+} is the dominant cation contributing more than 50% to the cation budget. A few springs show Mg^{2+} or Na^+ as a dominant cation. Among the anions, HCO_3^- is the most

Figure 8. Langlier-Ludwig plot showing the possible dissolution trends.

abundant contributing $>50\%$ to anion budget in all types of waters except some samples from glacier melt, the stream fed by the glacial melt and snow melt. A few streams and glacial melt were dominated by SO_4^{2-} . Cl^- is the least abundant anion. A little bit of enrichment of Na^+ in May seems to be due to the recharged snow melt through silicate rocks, as the periphery of the study area is dominated by the silicate rocks.

Spring water and stream water samples were plotted on a Piper trilinear diagram (figure 6). The order of four hydrochemical water types identified is $\text{Ca-HCO}_3 > \text{Ca-Mg-HCO}_3 > \text{Mg-HCO}_3 > \text{Na-HCO}_3 > \text{Ca-SO}_4$ type. At higher altitudes, the dominant infiltrating recharge in the form of snow melt, glacial melt and precipitation were found to be of Ca-HCO_3 type with the exception of glacial melt which was Ca-SO_4 type. As the water infiltrates and moves downgradient, more and more

chemical constituents are added and the groundwater evolves and modifies to different water types depending upon its flow path and the host lithology. In the present study, four such important water evolutions were observed. Ca-HCO_3 , Ca-Mg-HCO_3 and Mg-HCO_3 are the most common and expected water types resulted from the congruent dissolution of carbonate hosted lithology. Na-HCO_3 water type, followed by the warm springs owing to their long circuitous route and interaction with multiple lithology, resulted from incongruent dissolution of silicate rocks and congruent dissolution of carbonate rocks. Unlike groundwater, the evolution of surface water is observed to be simple with all the streams changed in to Ca-HCO_3 water type due to easy dissolution of carbonate minerals, less time for water-rock interaction and short route to flow.

4.4 Geochemical processes controlling water composition

The major ion chemistry of groundwater is a powerful tool for determining solute sources and for describing water evolution as a result of water-rock interaction leading to the dissolution of carbonate minerals, and silicate weathering and ion exchange processes (Herczeg *et al* 1991; Hiscock 1993; Kimblin 1995; Elliot *et al* 1999; Edmunds and Smedley 2000; Jeelani and Shah 2006).

Ca/Mg molar ratios in the surface and spring waters of SE Kashmir Valley (table 2) averages ~ 6 (0.4–17) and ~ 2.6 (0.43–8.53), respectively. In the surface water samples, the molar ratios are high in November and low in March, while in groundwater samples the molar ratios are high in March/July and low in May. The high variability of the Ca/Mg molar ratio in surface waters indicates various sources of Ca^{2+} and Mg^{2+} (carbonates, silicates) evaporate at different seasons. As all the water samples are undersaturated with calcite

Figure 9. PCO_2 vs. SI_{cal} ; PCO_2 vs. SI_{dol} and SI_{cal} vs. SI_{dol} showing geochemical behaviour of groundwater with the change in seasons.

Table 3. Summary of saturation indices of calcite and dolomite and PCO_2 of karst springs of study area.

Sampling date & no.	Statistics	SI_c	SI_d	PCO_2
November 2007, N = 13	Min	-0.1	-0.2	0.0001
	Max	1.7	2.6	0.0012
	Mean	0.9	1.2	0.0004
	SD	0.5	0.8	0.0004
March 2008, N = 19	Min	-1.8	-4.0	0.0017
	Max	0.1	-0.2	0.0457
	Mean	-0.7	-2.1	0.0148
	SD	0.6	1.2	0.0111
May 2008, N = 20	Min	-1.5	-3.3	0.0004
	Max	0.1	0.3	0.0174
	Mean	-0.7	-1.8	0.0068
	SD	0.6	1.1	0.0055
July 2008, N = 22	Min	-1.2	-3.5	0.0005
	Max	0.9	1.3	0.0646
	Mean	-0.3	-1.2	0.0129
	SD	0.5	1.1	0.0136

and dolomite, the variation in Ca/Mg molar ratio seems to be dependent on the lithogenic source. Low molar ratio is attributed to the weathering of silicates and/or dolomite, and high molar ratios can result from calcite weathering. The plot Ca/Mg *vs.* Mg (figure 7) shows the decrease of the molar ratio with the increase in Mg^{2+} concentration indicating the source of Ca^{2+} and Mg^{2+} from dolomite weathering.

In Ca/(Ca+Mg) *vs.* $SO_4/(SO_4+HCO_3)$ plot (figure 7) all the surface water and most of the spring water samples are characterized by high Ca/(Ca+Mg) molar ratio indicating that the waters react mainly with calcite. However, the spring waters with intermediate values indicate the interaction with dolomite as well particularly in May when the recharge due to the snow melting is at its peak. The Ca/(Ca+Mg) molar ratio of 0.5 and 1 correspond to the dissolution of stoichiometric dolomite and pure calcite, respectively (Fronzini 2008). The relative increase in Mg with the increase in SO_4^{2-} , in stream water samples, suggests the simultaneous process of dedolomitization and the gypsum and/or anhydrite dissolution.

In the Langlier–Ludwig plot (figure 8), the snow and glacier melt, surface water and the spring water are characterized by three main trends: I (dissolution of gypsum/anhydrite), II (carbonate dissolution) and III (silicate dissolution). The plot shows that most of the spring waters and a few streams are dominated by the carbonate dissolution with $Ca(Mg)HCO_3$ as the principal water type observed in most of the karst springs and streams of Anantnag. Most of the streams and snow and glacial melt are dominated by the gypsum dissolution. However, some springs attained the

Na– HCO_3 type by the incongruent dissolution of silicates. These springs are typical warm springs which though emerge throughout the carbonate lithology, interact with other silicate lithology at different levels of flow path. The increase of Na + K with the decrease of Ca + Mg in period of maximum flow and recharge is attributed to the infiltration of recharged snow/glacial melt and even rain, through diverse lithology particularly silicate rocks.

4.5 PCO_2 , SI_{cal} and SI_{dol} of karst springs

The PCO_2 is a very significant parameter and most important source for the enhanced solubility in carbonate rocks. In the soil zone, CO_2 is respired by the plants (~40%) and soil fauna, micro fauna and micro flora (>50%) (Ford and Williams 2007). In open systems, the soil CO_2 reacts with the descending or infiltrating waters to produce consistent supply of carbonic acid. The PCO_2 and saturation indices for calcite (SI_{cal}) and dolomite (SI_{dol}) were computed using the following equations (after Ford and Williams 2007):

$$\log PCO_2 = \log(HCO_3^-) - pH + pKCO_2 + pK_1$$

$$SI_{cal} = \log(Ca^{2+}) + \log(HCO_3^-) + pH - pK_2 + pK_{cal}$$

$$SI_{dol} = \log(Ca^{2+}) + \log(Mg^{2+}) + 2\log(HCO_3^-) + 2pH - 2pK_2 + pK_{dol}$$

where, pK_1 , pK_2 , $pKCO_2$, pK_{cal} , pK_{dol} are equilibrium constants for carbonate dissolution system. The computed values range from ($10^{-4} \times 6.92$)

to ($10^{-1} \times 2.29$) which is higher than the atmospheric PCO_2 ($10^{-3.5}$) and lie in the range of soil PCO_2 values, except springs in November (figure 9, table 3). This suggested that the karst system is open and the waters are highly aggressive in March, May and July, capable of dissolving carbonate rocks. The spring waters during these seasons are undersaturated with respect to calcite and dolomite. It is pertinent to mention here that the recharge is active during these seasons due to snow and glacier melting and rains. However, in November (winter season) the recharge is negligible due to frozen temperatures which make the karst system as a closed system. During this season the spring waters are not aggressive as the carbonic acid is consumed and not replenished, leaving the waters saturated with respect to calcite and dolomite. The plot SI_{cal} vs. SI_{dol} (figure 9, last panel) shows a very good correlation between SI_{cal} and SI_{dol} reflecting the simultaneous dissolution of calcite and dolomite in all the seasons with different rate of dissolution being higher in calcite and lower in dolomite.

5. Conclusions

The surface and spring waters of SE Kashmir are cold, moderately alkaline with low TDS. In general, the abundance of solutes in the surface waters is lower than the spring waters with Ca^{2+} and Mg^{2+} as dominant cations and HCO_3^- as dominant anion. Ca-HCO_3 , Ca-Mg-HCO_3 and Mg-HCO_3 water types suggest the carbonate lithology as the dominant host rock. Na-HCO_3 water type demonstrates the interaction of water with silicate lithology and longer circuitous route followed by the warm springs. Congruent carbonate dissolution (calcite dissolution, dedolomitization) and incongruent silicate weathering were found to be the dominant processes controlling the spring water chemistry. The unsaturated nature of spring water with respect to calcite and dolomite in most of the seasons make the waters aggressive. The results also revealed that some karst springs are recharged by the streams; Achabalnag is recharged by the Bringi stream, Andernag and Martandnag by Liddar stream.

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References

- Akdim B and Amyay M 1999 Environmental vulnerability and agriculture in the karstic domain: Landscape indicators and cases in the Atlas Highlands Morocco; *Int. J. Speleol.* **28B** 119–138.
- APHA, AWWA, WEF 2001 *Standard methods for the examination of water and waste water* (APHA-AWWA-WEF Washington).
- Bonaccio 2004 Hazards caused by natural and anthropogenic changes of catchment area in karst; *Nat. Hazards Earth Syst. Sci.* **4** 655–661.
- Burri E, Castiglioni B and Sauro U 1999 Agriculture, landscape and human impact in some karst areas of Italy; *Int. J. Speleol.* **26** 33–54.
- Calò F and Parise M 2006 Evaluating the human disturbance on karst environments in Southern Italy; *Acta Carsologica* **35** 47–56.
- Christman M C and Culver D C 2001 The relationship between cave biodiversity and available habitat; *J. Biogeogr.* **28** 367–380.
- Coward J M H, Waltham A C and Bowser R J 1972 Karst springs in the Vale of Kashmir; *J. Hydrol.* **16** 213–223.
- Dalai T K, Krishnaswami S and Sarin M M 2002 Major ion chemistry in the headwaters of the Yamuna river system: Chemical weathering, its temperature dependence and CO_2 consumption in the Himalaya; *Geochim. Cosmochim. Acta* **66** 3397–3416.
- Delle Rose M, Parise M and Andriani G F 2007 Evaluating the impact of quarrying on karst aquifers of Salento (southern Italy); In: *Natural and Anthropogenic Hazard in Karst Areas* (eds) Parise M and Gunn J; *Geol. Soc. London* **279** 153–171.
- De Waele J and Follesa R 2004 Human impact on karst: The example of Lusaka (Zambia); *Int. J. Speleol.* **32** 71–84.
- Drever J I 1988 *The geochemistry of natural waters* (Prentice Hall: New Jersey), 436p.
- Edmunds W M and Smedley P L 2000 Residence time indicators in groundwater: The East Midlands Triassic sandstone aquifer; *Appl. Geochem.* **15** 737–752.
- Elliot T, Andrews J N and Edmunds W M 1999 Hydrochemical trends, paleorecharge and groundwater ages in the fissured Chalk aquifer of the London and Berkshire basins, UK; *Appl. Geochem.* **14** 333–363.
- Ford D and Williams P 2007 *Karst geomorphology and hydrology* (Unwin Hyman: London), 608p.
- Fronchini F 2008 Geochemistry of regional aquifer systems hosted by carbonate-evaporite formations in Umbria and southern Tuscany (central Italy); *Appl. Geochem.* **23** 2091–2104.
- Frumkin A 1999 Interaction between karst, water and agriculture over the climatic gradient of Israel; *Int. J. Speleol.* **28B** 99–110.
- Gams I, Nicod J, Julian M, Antony E and Sauro U 1993 Environmental change and human impacts on the Mediterranean karsts of France, Italy and the Dinaric region; *Catena Suppl.* **25** 59–98.
- Ginés A 1999 Agriculture, grazing and land use changes at the Serra de Tramuntanakarstic mountains; *Int. J. Speleol.* **28B** 5–14.
- GSI 1977 Geology and mineral resources of states of India, part X: Jammu and Kashmir State; *Geol. Surv. India* **30** 1–70.
- Gunn J 2007 Contributory zone definition for groundwater source protection and hazard mitigation in carbonate aquifers; In: *Natural and anthropogenic hazards in karst areas* (eds) Parise M and Gunn J, *Geol. Soc. London*, vol. 279.

- Han G and Liu C Q 2004 Water geochemistry controlled by carbonate dissolution: A study of the river waters draining karst dominated terrain, Guizhou Province, China; *Chem. Geol.* **204** 1–21.
- Herczeg A L, Torgersen T, Chivas A R and Habermehl M A 1991 Geochemistry of groundwaters from the Great Artesian Basin, Australia; *J. Hydrol.* **126** 225–245.
- Hiscock K M 1993 The influence of pre-Devensian deposits on the hydrogeochemistry of the Chalk aquifer system of north Norfolk, UK; *J. Hydrol.* **144** 335–369.
- Hunkeler D and Mudry J 2007 Hydrochemical methods; In: *Methods in karst hydrogeology* (eds) Goldscheider N and Drew D, Taylor and Francis, pp. 93–121.
- Jeelani G 2005 Chemical quality of the spring waters of Anantnag, Kashmir; *J. Geol. Soc. India* **66** 453–462.
- Jeelani G 2007 Hydrogeology of hard rock aquifer in Kashmir Valley: Complexities and uncertainties; In: *Groundwater dynamics in hard rock aquifers – including sustainable management and optimal monitoring network design* (eds) Ahmed S, Jayakumar R and Abdin S (Netherlands: Springer Verlag) 265p.
- Jeelani G 2008 Aquifer response to regional climate variability in a part of Kashmir Himalaya in India; *Hydrogeol. J.* **16** 1625–1633.
- Jeelani G and Shah A Q 2006 Geochemical characteristics of water and sediment from the Dal Lake, Kashmir Himalaya, India: Constraints on weathering and anthropogenic activity; *Env. Geol.* **50** 12–23.
- Juberthie C and Decu V (eds) 1994 *Encyclopedia Biospeologia, Moulis France*; Societe de Biospeologie, 834p.
- Kacaroglu F 1999 Review of groundwater pollution and protection in karst areas; *Water Air Soil Poll.* **113** 337–356.
- Karim A and Veizer J 2000 Weathering processes in the Indus River Basin: Implications from riverine carbon, sulfur, oxygen, and strontium isotopes; *Chem. Geol.* **170** 153–177.
- Kimblin R T 1995 The chemistry and origin of groundwater in Triassic sandstone and Quaternary deposits, north-west England and some UK comparisons; *J. Hydrol.* **172** 293–311.
- Krishnaswami S, Singh S K and Dalai T K 1999 Silicate weathering in the Himalaya: Role in contributing to major ions and radiogenic Sr to the Bay of Bengal; In: *Ocean Science, Trends and Future Directions* (ed.) Somayajulu B L K, Indian National Science Academy and Akademia International, New Delhi, pp. 23–51.
- Latham A G, McKee J K and Tobias P V 2007 Bone breccias, bone dumps, and sedimentary sequences of the western Limeworks, Makapansgat, South Africa; *J. Hum. Evol.* **52** 388–400.
- Middlemiss C S 1910 Revision of Silurian-Trias sequence of Kashmir; *Rec. Geol. Surv. India* **40** 206–260.
- Middlemiss C S 1911 Sections in the PirPanjal range and Sindh Valley, Kashmir; *Rec. Geol. Surv. India* **41** 115–144.
- Milanovic P T 2001 *Geological Engineering in Karst* (Zebra Publishing: Belgrade) 347p.
- Négrel P, Allègre C J, Dupré B and Lewin E 1993 Erosion sources determined by inversion of major and trace element ratios in river water: The Congo Basin case; *Earth Planet. Sci. Lett.* **120** 59–76.
- Nicod J, Julian M and Anthony E 1997 A historical review of man–karst relationships: Miscellaneous uses of karst and their impact; *Riv. di. Geog. Ital.* **103** 289–338.
- Palmer A N 1991 Origin and morphology of limestone caves; *Geol. Soc. Am. Bull.* **103** 1–21.
- Parise M and Pascali V 2003 Surface and subsurface environmental degradation in the karst of Apulia southern Italy; *Env. Geol.* **44** 247–256.
- Parise M and Gunn J 2007 *Natural and anthropogenic hazards in karst areas*; Geol. Soc. London, 279p.
- Potter P E 1978 Petrology and chemistry of big river sands; *J. Geology* **86** 423–449.
- Quade J, English N and DeCelles P G 2003 Silicate versus carbonate weathering in the Himalaya: A comparison of the Arunand Seti River watersheds; *Chem. Geol.* **202** 275–296.
- Sarin M M, Krishnaswami S, Dilli K, Somayajulu B L K and Moore W S 1989 Major ion chemistry of the Ganga–Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal; *Geochim. Cosmochim. Acta* **53** 997–1009.
- Sasowsky I D 2007 Clastic sediments in caves – imperfect recorders of processes in karst; *Acta Carsologica* **36** 143–149.
- Sauro U 1993 Human impact on the karst of the Venetian Fore-Alps, Italy; *Env. Geol.* **21** 115–121.
- Sauro U 2006 Changes in the use of natural resources and human impact in the karst environment of the Venetian Prealps (Italy); *Acta Carsologica* **35** 57–63.
- Singh S K, Trivedi J R, Pande K, Ramesh R and Krishnaswami S 1998 Chemical and Sr, O, C, isotopic compositions of carbonates from the Lesser Himalaya: Implications to the Sr isotope composition of the source waters of the Ganga, Ghaghara and the Indus Rivers; *Geochim. Cosmochim. Acta* **62** 743–755.
- Singh S K, Sarin M M and France-Lanord C 2005 Chemical erosion in the eastern Himalaya: Major ion composition of the Brahmaputra and $\delta^{13}\text{C}$ of dissolved inorganic carbon; *Geochim. Cosmochim. Acta* **69** 3573–3588.
- Smith D I 1993 The nature of karst aquifers and their susceptibility to pollution; *Catena Suppl.* **25** 41–58.
- Spizzico M, Lopez N and Sciannamblo D 2005 Analysis of the potential contamination risk of groundwater resources circulating in areas with anthropogenic activities; *Nat. Haz. Earth Syst. Sci.* **5** 109–116.
- Urich P B 2002 Land use in karst terrain: Review of impacts of primary activities on temperate karst ecosystems; *Sci. Conser.* **198** 5–60.
- Wadia D N 1975 *Geology of India* (Tata McGraw Hill: New Delhi), 560p.
- White W B 1988 *Geomorphology and hydrology of karst terrains* (Oxford University Press: New York), 462p.
- White W B 2004 Paleoclimate records from speleothems in limestone caves; In: *Studies of cave sediments: Physical and chemical records of paleoclimate* (eds) Sasowsky I D and Mylroie J E (New York: Kluwer Publishers), pp. 135–176.
- White W B 2007 Cave sediments and paleoclimate; *J. Cav. Kar. Stud.* **69** 167–93.
- Williams P 1993 Karst terrains, environmental changes and human impacts; *Catena Suppl.* **25** 268p.