Hydrochemical Characteristics of Some Typical Freshwater Springs - A Case Study of Kashmir Valley Springs

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Abstract: In the recent years the rapid development activities has inflicted significant pressures on fresh waters which has created increased demand for water likely to be fulfilled by ground water. The concentration of nutrients in groundwater acts as an indicator to identify the influence of agriculture activities and other land use patterns. In this backdrop a field study was conducted to assess variations in physico-chemical characteristics of water of the seven springs being used for multipurpose which revealed that these springs are hard water with the predominance of bicarbonate and calcium than other ions and best suited for drinking purposes. Fair to substantial spatial and temporal variations in water temperature, pH, conductivity, dissolved oxygen, hardness, calcium, alkalinity, potassium, nitrate nitrogen, sulphate and phosphorus were observed among the springs under study. Springs having varied immediate catchment displayed varied hydrochemistry. Springs like Verinag, Sherebagh, Indraznag and Cheshmashahi are of limnocrene while Kokernag and Achabal fall under rheocrene and Dobinag under helocrene as per Theineman classification of springs. Similarly on the basis of magnitude of discharge, springs viz. (i) Kokernag and Achabal, (ii) Verinag and Sherebagh, (iii) Dobinag and (iv) Indraznag and Cheshmashahi plunge in the spring order 2, 3, 4 and 5 respectively.

Key words: Hydrochemical characteristics • Spatio-temporal variations • Freshwater springs • Kashmir Himalaya • Land use pattern

INTRODUCTION

Globally, springs are disappearing at an alarming rate and most of that loss goes largely unrecognized and our valley is no more exception to this trend and the situation is more alarming in light of climate change predictions for Himalaya. National efforts are needed to bring attention to the ecological importance of springs and their conservation. The population of Jammu and Kashmir like other parts of India is witnessing an enormous growth in human population and supply of drinking water seems to be a real challenge. Without investment in intensive research and effective public distribution system the per capita demand for potable water is likely to remain a dream. In this backdrop a field study was conducted to assess variations in physico-chemical characteristics of water of the springs located within the three districts namely Anantnag, Pulwama and Srinagar of the Kashmir valley wherein the water is being used for many purposes like drinking, swimming, irrigation, washing/bathing, recreation, fishery etc.

Karstic terrains cover approximately 12% of the earth’s continental surface and 25% of the world’s population is dependent on water supply partially or entirely coming from freshwater springs [1]. One of the most pressing issues the world faces is the management of freshwater resources amongst which springs have become a focal points because of their geological, ecological, scientific, cultural and societal importance besides burgeoning demands for drinking, irrigation, industrial, fishery and recreational purposes in different parts of the world [2]. The intensive agriculture, domestic sewage and other land use patterns have impaired the quality of spring waters by contributing large quantities
of nutrients to groundwater recharge \[3, 4, 5, 6\]. The physical environment of springs is determined by its geomorphological setting while as the aquifer and emergent surface terrain dictate discharge, temperature, water chemistry, dissolved oxygen concentration, substrate, habitat permanence and organic matter levels \[7, 8\]. The number of springs is not exactly known for most geographical regions and those few regional estimates that have been made vary by over three orders of magnitude. These numbers are underestimates as they are based on surveys that usually ignore small springs and seeps, which greatly exceed the number of larger springs. Therefore, keeping in view the abundance of springs, they happen to play key role in part of the hydrologic cycle \[9, 10, 11\]. In spite of being one of the main components in the longitudinal zonation of lotic systems, spring habitats have received much less attention than lakes and streams/rivers and are still widely understudied. However, springs, are seriously threatened by several direct and indirect impacts, the most important being their capture to obtain drinking water, hydroelectric power, fisheries, encroachment etc. Throughout the world there is a growing recognition of the value of springs and several initiatives have been implemented to ensure their protection and sustainable management \[12, 13, 14, 15\]. The goal is to provide water for the environment to sustain and where necessary restore ecological processes and biodiversity of Groundwater Dependent Ecosystems (GDEs) such as springs. The valley of Kashmir is known for its extensive springs habitats which often exhibited physico-chemical condition that contrast greatly to surface fed streams. These unique habitats are usually characterized by a stable discharge regime, constant temperatures, elevated but stable levels of ionic enrichment and sometimes low levels of dissolved oxygen. Springs in Valley of Kashmir are essentially unexplored and the information regarding the various hydrochemical attributes is scant, if it exists at all because they are almost undescribed and understudied.

**Geological and Hydrogeological Characteristics of the Study Area:** The high altitude valley of Kashmir is an ovoid basin with a nearly flat floor of around 4920 km\(^2\) and is existing between the lesser and greater Himalayas. The valley of Kashmir with tectonic origin now lies in Indian occupied Kashmir is 135 km long and 45km broad at its middle, lying as an oval bowl between the Zanaskar range to the North and Pir Panjal range to the South. The valley is surrounded on all sides by high mountains which remains snow-clad for most of the year. The valley abounds in snow-fed, spring-fed streams, rivers with a network of their tributaries and numerous freshwater lakes. Most of the valley lies at an elevation of just over 1500m, though its floor rises steadily from northwest to southwest \[16\]. The valley of Kashmir is drained by the river Jhelum which leaves it through a deep gorge in its northwest cones. The valley of Kashmir being surrounded by Himalayan ranges resembles the Mediterranean type being characterized by a rainfall occurring throughout the year except 2-3 dry periods in summer and autumn. Kashmir valley experienced about 635-680 mm rainfall (2004-05) with maximum average monthly temperature of about 20.45°C having monthly average extremes ranging from -3.3°C in December 2005 to 30.4°C in August 2005 recorded in capital city Srinagar \[17\].

The valley of Kashmir harbours hundreds of springs of different magnitudes which attract the tourists and play important role in formation of landscape, rearing of fish, irrigation and drinking water (Table 1). Seven freshwater springs falling in three districts of valley namely Srinagar (Cheshmashahi), Anantnag (Verinag, Kokernag, Achabal and Sherebagh) and Pulwama (Indraznag and Dobinag) were selected for the purpose of present study (Table 2, Figure 1).

Kashmir valley one of the many NW-SE oriented depressions of regional dimensions of Himalayan mountain systems is an intermontane valley bounded by four major ranges (Pir Panjal range, Saribal range, Great Himalayan range and Qazinag range). The valley itself occupies the core of a slightly basinal synclinorium where Triassic rocks are surrounded by Paleozoic series and are overlain by Pleistocene and recent sediments. Upper paleozoic rocks, lavas, pyroclastics and arenites are only marginal to the Anantnag area although they do support most of the drainage head waters. Karst is commonly considered as the result of the solution process of carbonate rocks (limestone and dolomite).The limestone is by no means pure and contains from 15-90% dolomite with the higher values being more spread. It is generally a very fine carbonate mosaic with small proportions of fossil fragments and mainly Ferruginous insoluble grains. Despite of this, the most carbonate rocks are karstified and an important source of large freshwater springs. The Pleistocene beds form the Krewa series and alluvial plains comprising mainly fine lacustrine sandstones.
Table 1: Water usage category of different studied springs

<table>
<thead>
<tr>
<th>Spring</th>
<th>Drinking</th>
<th>Irrigation</th>
<th>Washing/Bathing</th>
<th>Fishery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verinag</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
<td>Kokernag</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Achabal</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Sherebagh</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
<td>Indragn</td>
<td>_</td>
<td>+++</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>Dobinag</td>
<td>_</td>
<td>+++</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>Cheshmashahi</td>
<td>+++</td>
<td>_</td>
<td>_</td>
<td>_</td>
</tr>
</tbody>
</table>

+++ = High water use; ++ = Moderate water use; + = Low water use; — = Negligible water use

Table 2: General Characteristics of studied springs

<table>
<thead>
<tr>
<th>Sites</th>
<th>Latitude (N)</th>
<th>Longitude (E)</th>
<th>Altitude (m)</th>
<th>Average Depth (m)</th>
<th>Catchment</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verinag</td>
<td>33°32.128'</td>
<td>75°15.036'</td>
<td>1839</td>
<td>15</td>
<td>Forest</td>
<td>Domestic</td>
</tr>
<tr>
<td>Kokernag</td>
<td>33°35.202'</td>
<td>75°17.926'</td>
<td>1922</td>
<td>0.5</td>
<td>Forest</td>
<td>Domestic</td>
</tr>
<tr>
<td>Achabal</td>
<td>33°40.954'</td>
<td>75°13.395'</td>
<td>1663</td>
<td>0.5</td>
<td>Forest</td>
<td>Domestic</td>
</tr>
<tr>
<td>Sherebagh</td>
<td>33°43.916'</td>
<td>75°09.325'</td>
<td>1617</td>
<td>1.2</td>
<td>Forest/residential</td>
<td>Domestic</td>
</tr>
<tr>
<td>Indragn</td>
<td>33°54.341'</td>
<td>74°54.199'</td>
<td>1604</td>
<td>0.4</td>
<td>Agricultural</td>
<td>Irrigation</td>
</tr>
<tr>
<td>Dobinag</td>
<td>33°48.574'</td>
<td>74°51.367'</td>
<td>1804</td>
<td>0.5</td>
<td>Agricultural</td>
<td>Irrigation/Fisheries</td>
</tr>
<tr>
<td>Cheshmashahi</td>
<td>32°35.870'</td>
<td>75°21.120'</td>
<td>1686</td>
<td>0.5</td>
<td>Forest</td>
<td>Drinking</td>
</tr>
</tbody>
</table>

Fig. 1: Location map of the study area showing various selected freshwater springs
In between the limestone ridges and Karewa terraces is embedded a thick bed of alluvium mainly of coarse gravel and boulders. Karst features are not fully developed in the Triassic limestone because of high dolomite content [18]. Due to diversified geological formations, lithological variations, tectonic complexity etc the valley is usually characterized by soft rocks (Karewas and alluvium) and hard rock (Panjal traps and Triassic limestones).

MATERIALS AND METHODS

In order to measure the detailed hydrochemical variations, seven freshwater springs falling in three districts of Kashmir valley namely Srinagar (Cheshmashahi), Anantnag (Verinag, Kokernag, Achabal and Sherebagh) and Pulwama (Indraznag and Dobinag) were chosen for present study. The samples were obtained near spring bowl and processed on monthly basis however it is extremely difficult to handle large amount of data and taking this thing into consideration the seasonal and annual mean values of different parameters are presented in the paper. The parameters like water temperature, pH and conductivity were measured with digital thermometer, pH metre and conductivity metre respectively while dissolved oxygen was estimated by Winkler’s titration method [19, 20]. The parameters like chloride (Argentimetric), alkalinity (Titrimetric) and hardness (EDTA titrimetric method) were measured by titrimation methods while ammonical nitrogen (Phenate method), nitrate (Sodium salicylate), phosphorus (Ascorbic acid), dissolved silica (Molybdate blue), sulphate (Turbidimetric method) and sodium and potassium were analysed by spectrophotometric and flame photometric methods respectively [19, 20]. Geocoordinates and elevations were determined with GPS and the Tukey’s HSD was employed through SPSS.

RESULTS AND DISCUSSION

The chemical composition of groundwater results from the geochemical processes occurring as water reacts with the geologic materials through which it flows. In addition, the land use or human activities within the catchment can affect the groundwater quality. Following the Theineman classification of springs [21], springs like Verinag, Sherebagh, Indraznag and Cheshmashahi were considered as limnocrene while Kokernag and Achabal fall under rheocrene and Dobinag under helocrene (Table 3.) Similarly on the basis of magnitude of discharge employing the Meinzer classification of springs [22], the various types of springs viz. (i) Kokernag and Achabal, (ii) Verinag and Sherebagh, (iii) Dobinag and (iv) Indraznag and Cheshmashahi plunge in the spring order 2, 3, 4 and 5 respectively while as the classification given by Rosenau puts these on the same spring order excepting Verinag which falls under spring order 2 instead of spring order 3 [23]. Based on the hydraulic characteristics and character of opening, the springs under study proved to be artesian and fracture type excepting Dobinag which is of nonartesian and filtration type. Further, the springs under study happen to fall under cold water springs as per the classification given by some workers [22, 24] except Sherebagh spring where annual mean water temperature (16.55±0.47°C) was slightly higher than the annual mean air temperature. The mean annual mean water temperature oscillated between 10.72±1.0°C (Kokernag) and 16.55±0.47°C (Sherebagh) amongst the springs. The springs under study are at intermediate elevations (1400-2100m) and probably meet the definition of cold springs except Sherebagh. The slightly constant and higher water temperature of Sherebagh is probably due to longer circulation paths but the slightly anomalous temperature of Sherebagh may also be due to conductive heat transfer rather than any volcanic activity involving a hydrothermal system [25]. The variation in annual air temperatures seems behind the sinusoidal pattern in spring water temperatures with maxima in summers and minima in winters [26].

The pH of the spring waters reflected from seasonal mean values (Figure 2) was on the alkaline side excepting Indraznag and Dobinag. The slightly acidic character of these two springs, unlike other springs, is because of their different catchment and macrophyte dominance. Higher concentration of sulphates in these two springs, related to the presence of pyrite in the catchment and decomposition of macrophytes releasing organic acids and diurnal changes in the dissolved free carbon dioxide are probably the causal factors for lowering the pH values of the springs. The variation in the pH values from one season to another is generally related to dilution, due to influx of rain water in the recharge zone of aquifer. The conductivity of the spring waters exhibited variations within the range of 147±18.34 IS/cm (Dobinag)-375±48.53 IS/cm (Sherebagh). The lowest seasonal mean values of conductivity were obtained in winter for most of the springs. The possible reason for such a trend is due to the dilution factor as there was a heavy snowfall during the winter as the same has been reported elsewhere [27]. The springs relatively at higher altitudes depicted lower
Table 3: General Physical attributes of studied springs

<table>
<thead>
<tr>
<th>Sites/Springs</th>
<th>Discharge(mean) (L/sec)</th>
<th>Spring Order</th>
<th>Spring Type</th>
<th>Hydraulic</th>
<th>Topography</th>
<th>Substrate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verinag</td>
<td>842</td>
<td>3</td>
<td>2</td>
<td>Artesian</td>
<td>Limnocrene</td>
<td>Cobble, Gravel, Sand, Mud etc</td>
</tr>
<tr>
<td>Kokernag</td>
<td>1371</td>
<td>2</td>
<td>2</td>
<td>Artesian</td>
<td>Rheocrene</td>
<td>Cobble, Pebble, Sand, Leaf litter etc</td>
</tr>
<tr>
<td>Achabal</td>
<td>1012</td>
<td>2</td>
<td>2</td>
<td>Artesian</td>
<td>Rheocrene</td>
<td>Cobble, Pebble, Mud, Sand, etc</td>
</tr>
<tr>
<td>Sherbagh</td>
<td>199</td>
<td>3</td>
<td>3</td>
<td>Artesian</td>
<td>Limnocrene</td>
<td>Gravel, Sand, Mud, Organic Detritus, etc</td>
</tr>
<tr>
<td>Indraznag</td>
<td>4.5</td>
<td>5</td>
<td>5</td>
<td>Artesian</td>
<td>Limnocrene</td>
<td>Mud, Sand, Organic detritus, etc</td>
</tr>
<tr>
<td>Dobinag</td>
<td>3.5</td>
<td>5</td>
<td>5</td>
<td>Gravity/Non Artesian</td>
<td>Helocrene</td>
<td>Mud, Organic detritus, etc</td>
</tr>
<tr>
<td>Chesmashahi</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>Artesian</td>
<td>Limnocrene</td>
<td>Cement Bed</td>
</tr>
</tbody>
</table>

annual mean values of conductivity as compared to those at lower altitude with the exception of Verinag which may be due to the higher discharge of water, a fact also supported by other study [28]. Data obtained on dissolved oxygen concentrations depicted considerable spatial variations from 1.78±0.58 mg/L at Sherbagh to 6.76±1.68 mg/L at Kokernag. The slight increase in the concentration of dissolved oxygen during the summers is due to photosynthetic activity in the springs. The striking feature connected with dissolved oxygen of springs under study is its nearly constant concentrations exhibited through the study period (Figure 2).

Apparently the water, which has just emerged from subterranean cervices and is fairly homogenous with respect to dissolved oxygen content, does not remain in contact with the plants of the spring bowl area for a sufficient length of time to allow an increase in dissolved oxygen content due to photosynthetic activity. Apart from Sherbagh and Indraznag, the rest of the springs displayed the fair amount of oxygen which is in consonance with the findings of other investigators [29, 30]. Further, the relatively high nutrient level in Sherbagh also interferes with the solubility of oxygen though very passively, thereby decreasing the oxygen concentrations. In general, the spatial characteristics (macrophyte dominance and photosynthetic activity) of individual springs besides water temperature does have an impact on temporal fluctuations of dissolved oxygen in different springs (Figure 2). The relatively lesser concentration of dissolved oxygen at Sherbagh and Indraznag is attributed to slightly warm conditions and to some extent the macrophyte dominance at Indraznag which consumes oxygen during decomposition thereby rendering its concentration to be low. The higher values of dissolved oxygen concentration were observed in spring season (comparatively at Verinag and Kokernag) possibly because of the low water temperatures. The decrease in the dissolved oxygen concentration at Indraznag and Sherbagh during the summer is due to slight increase in water temperature because of increase in biochemical reactions which consume dissolved oxygen at a rapid rate, thus rendering its concentration to be lower in summer [31].

The waters, in general, were rich in free CO₂ because of dissolution of carbonates from the catchment. Besides, underground waters usually contain large amounts of carbon dioxide because of decomposition of organic matter and bacterial respiration in the soil as well as its percolation and passage through limestone [32]. The lower concentration of free CO₂ reported in spring season is due to heavy rainfall which in turn is responsible for the dilution effects by rain water via karst conduit and overlying catchment thereby rendering its concentration to the lower levels. On the other hand, relatively low rainfall in autumn followed by winter and summer seasons has a direct bearing on the increased CO₂ concentration due to dissolving of CO₂ into infiltrating rain water which feed the spring catchments [33, 26]. The alkalinity of water was mainly due to bicarbonates in all the springs which ranged between 103±20.91 mg/L (Dobinag) and 214±16.14 mg/L (Sherbagh). The seasonal variations in the bicarbonate alkalinity were significant as reflected from higher values during the summer season at most of the sites. The alkalinity increased with a decrease in altitude and also varied in different seasons. The maximum alkalinity was observed in summer and autumn and minimum during winter except Sherbagh. Addition of the carbon dioxide from rainwater (respiration by plant roots and microbial decomposition of organic matter) is the probable cause of increasing bicarbonate alkalinity during summer and autumn seasons [31]. There are differences in the alkalinity values according to the prevailing type of land use/recharge zones. The higher values of bicarbonate in agriculture than forested land-use have also been reported which also stand true though partially in the present study [34].
Fig. 2: Spatio-temporal variation in hydro-chemical features of seven springs (Mean±SD).
(V=Verinag; K=Kokernag; A=Achabal; S=Sherbagh; I=Indraznag; D=Dobinag; C=Cheshmashahi).
The hardness of the spring waters indicated their hard water nature with total hardness >150 mg/L CaCO3 equivalent except Cheshmashahi recording annual mean values < 100 mg/L. The maximum total hardness values, in general, were observed during autumn and winter. The springs at higher altitudes were observed to have comparatively lower hardness, while as an increase in hardness was noted in springs having agriculture land in immediate vicinity. The coefficient of variation (V) of total hardness ranged between 14% (Cheshmashahi) and 38% (Kokernag) which is considered indicative that these springs especially (Verinag, Kokernag, Achabal and Dobinag) are fast flowing water (conduit karst type) and therefore short contact residence time compared to Sherebagh, Indraznag and Cheshmashahi springs with coefficient of variation less than 20% which is considered partially typical of diffuse flow systems [35, 36]. Calcium and magnesium accounted for most of the hardness of water. The ions depicted a variation range of 26±6.29 mg/L (Dobinag and Cheshmashahi) to 61±12.30 mg/L (Cheshmashahi) to 14.33±8.19 mg/L (Dobinag) for magnesium. In general, the cationic composition of the spring waters revealed the predominance of calcium over the other ions [37] and, therefore, the usual cation progression obtained was Ca" >Mg" >Na" >K" except Sherebagh where magnesium gets replaced by sodium which brings it close to the well-known sequence for global freshwaters. The springs proved to be carbonate hosted as is indicated by the higher values of bicarbonate and lower dissolved silica. The spatial variability in water chemistry indicate the presence of short, localized flow as longer and less discrete paths could have created more uniform water chemistry spatially. The results suggest that the annual mean of calcium ion increased with decrease in altitude while the maximum values for calcium and magnesium were observed during winter as against the minimum in summer season. The marginal seasonal variations are possibly due to changes in base flow conditions through the bed rock. The annual mean concentration of sodium was lower than calcium at all the study sites. Among the sites studied, the maximum annual mean concentration was recorded for Sherebagh (41±21.86 mg/L) and minimum for Cheshmashahi (3±1.14 mg/L). Relatively higher concentration of sodium have been attributed to domestic as the Sherebagh spring is found in the midst of Anantnag city sewage [38]. Sodium ions in the springs are usually at lower concentrations except Sherebagh and the likely source of the sodium ions is probably the ion exchange when calcium ions from groundwater are replaced by sodium ions absorbed by clay rock particles [39]. Weathering of silicate rocks is one of the important processes responsible for higher concentration of sodium in the groundwater. Geochemically water in the Sherebagh can be classified as having a general Na/Cl composition as against the Ca-Cl composition in rest of the springs. Potassium was observed to be present in very low concentrations with a highest annual mean recorded at Sherebagh (5±3.66 mg/L) followed by Achabal (3.5±2.65 mg/L) and decreasing to the lowest at Cheshmashahi (1±0.41 mg/L) which are well within the range of values reported by [40]. Relatively low concentration of potassium in the spring waters may be due to the fixation in the form of clay minerals and greater resistance of potassium bearing minerals to weathering [41].

The chloride concentrations, in general, was found maximum during summer and spring while as winter and autumn depicted minimal concentrations of the ion for almost all the springs under study (Figure 1). The springs like Kokernag and Cheshmashahi at higher elevations depicted lower concentrations while as Indraznag and Sherebagh (comparatively at low altitudes) depicted highest chloride concentration. Considerable spatial variations in the chloride between different springs suggest a difference in the input level of impurities that contaminate the groundwater. No discernible seasonal trend was recorded in chloride concentration which suggests the cumulative effect of various factors operating at different springs however higher rainfall has been related elsewhere to the increased chloride concentrations in the spring-autumn seasons responsible for dissolution of more salts from water rock interaction. Further, the high chloride content in springs may be related to the presence of large amounts of organic matter of both allochthonous and autochthonous origin and contamination by sewage waste carrying detergents and sewage from human settlements especially Sherebagh. Both sulphate and sulphide occur in springs with sulphate being the dominant form. Concentrations of sulphate proved highly variable from 4±0.70 mg/L (Cheshmashahi) to 16±6.87 mg/L (Indraznag). Sulphate in carbonate rocks may be derived from dissolution of sulphate minerals (primarily gypsum and anhydrite) or oxidation of pyrite. Concentration of sulphate in the spring waters may be controlled by a study state.
dissolution process which perhaps gets influenced by biological sulphate. The springs at higher elevations usually registered relatively a bit higher concentrations than springs at lower elevations except Indraznag. The reason for low sulphate values in the studied springs may be attributed to rock formation being impregnated with low concentration of CaSO4 which is also reflected in the water chemistry especially when the water is issuing from underground sources [42]. Presence of ammonia in the water indicates pollution of recent origin whereas the nitrates in water suggests that some time has already elapsed during which nitrification has taken place and the water has got purified itself to some extent. Relatively higher concentrations of ammonia may be attributed to the release of ammonia from decomposition of algal mats, zooplankton and fishes which occur in higher densities at Sherebagh, Verinag and Dobinag. However, it is difficult to say precisely whether the main source of ammonia dissolved in the spring waters comes from bacterial mineralization of dead plants and animals or whether it is excreted by living animals. The NO3-N concentration varied between 560±236 ig/L (Cheshmashahi) –1534±1225 ig/L (Dobinag) throughout the study period. Relatively the higher concentration of nitrogen compounds may be due to domestic sewage which enters into groundwater through leaching from soil. In the present study, the domestic sewage near the springs seems a remote possibility except Sherebagh while as the agriculture activities and decomposition of organic matter remains the only sources of nitrogen in the recharge area. Storage of nitrate in the soil zone can delay and prolong the release of nitrate that is why less seasonal variations of nitrate concentrations in karst basins than nonkarst basins due to storage has been reported [44]. However, the isotopic studies have revealed that it is difficult to predict the nitrate concentration because of variability in source term and type of recharge. The variation in nitrate concentrations among the springs lying in the forests and agriculture catchments suggested a difference in input levels of nitrogen based fertilizers which lead to the contamination of the spring waters. Relatively higher levels of nitrate observed at Verinag, Indraznag and Dobinag indicate the influence of agriculture activities and decomposition of organic matter in terms of increased pollution and due to the application of urea as a major inorganic fertilizer. Lower nitrate concentrations have less possibility of contamination from agriculture wastes which in turn indicates the decomposition of living matter as a source of nitrate.

The springs usually contain only a minimal phosphorus levels because of the low solubility of native phosphate minerals and the well-known ability of the soils to retain phosphate. The relatively lower concentrations of phosphorus in spring waters is attributed to the strong bond formation of phosphate with clay minerals and metal hydroyxide as well as its involvement in biological cycle. The annual mean values of orthophosphorus and total phosphorus for the studied springs were in the range of 14±9.52 (Kokernag) to 46±12.31 ig/L(Sherebagh) and 130±58.99 (Verinag) to 497±225.13 ig/L (Sherebagh) respectively, which are higher than the values recorded in Irish Karst springs [45]. However, our results are well in consonance with study of Imbach [46] who reported concentration of phosphate ranging from 190-880 ig/L for karstic springs in the Çekirge-Bursa area of Turkey while another researcher reported concentration of phosphate ranging from 70-90 ig/L for the Pamukkale thermal karst springs in Turkey [47]. The spatial variations of phosphate concentrations indicate that springs having forested recharge zones usually recorded low concentrations as compared to Indraznag surrounded by agriculture fields while as the same is not true for Dobinag which is also surrounded by agriculture but having helo rare nature (Figure 3). Another probable reason is that springs like Verinag, Kokernag, Achabal and Sherebagh lie in the region covered by hard rock formation and thick weathered zone, whereas sedimentary formation mostly alluvium and sand occur near Indraznag and Dobinag.

The dissolved silica fluctuated but with a little constancy, exhibiting mean values between 4.5±0.89 mg/L (Kokernag) and 15±3.18 mg/L (Indraznag). The springs which recorded comparatively higher annual mean temperatures were found to contain higher concentration of dissolved silica. Dissolved silica has been reported with higher concentration in warm as compared to cold springs [47]. The cold (non-thermal springs) show a reasonably linear relation of increasing silica concentrations with increasing specific conductance that most likely reflects the degree of reaction with carbon dioxide, the major ion being bicarbonate which stands true for Sherebagh. Dissolved silica was the only parameter which was relatively at higher concentrations in Cheshmashahi thereby indicating the probable origin of silicate from dissolution of rocks within the catchment.
CONCLUSIONS

The geochemical signatures in the spring waters reflected the dominance of carbonate weathering while as the cationic composition of the spring waters revealed the predominance of calcium over the other ions and, therefore, the usual cation progression obtained was Ca\(^{++}\) >Mg\(^{++}\) >Na\(^+\) >K\(^+\) except Sherebagh where magnesium gets replaced by sodium. The results obtained suggest that these springs are dynamic and variable as reflected from their nutrient chemistry which showed marginal spatio-temporal variations. The variations at temporal scale are largely as the result of temperature and rainfall pattern besides other factors. In general, the spring water chemistry at Sherebagh shows trends indicating the possibility of percolation of polluted surface water which inturn influences the base flow through rocks. Results suggested that the anthropogenic influences (agriculture activities including application of fertilizers) are manifested in slightly acidic character, conductivity, free CO\(_2\), alkalinity, sodium, ammonia, nitrate and phosphate at Sherebagh, Indraznag and Dobinag. The springs at higher altitudes were observed to have comparatively lower hardness, while as an in increase in hardness was noted in springs having agriculture land in immediate vicinity. The coefficient of variation (V) of total hardness in general exceeds 5% for most of the springs which reflects that these springs are fast flowing water (conduit karst type) though with variable residence time periods. All the studied springs used for supplying mostly the drinking water were found to have good quality waters as per WHO guidelines and standards. In light of our observations, springs managers should consider promptly implementing inventory and assessment protocols, as well as immediate remedial response measures to cope with immediate threats to the spring ecosystems.

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