Chapter- 9

SYNTHESIS OF DATA AND CONCEPTUAL MODELING OF HYDROGEOCHEMICAL AND BACTERIOLOGICAL CHARACTERISTICS OF ANANTNAG SPRINGS
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It is imperative that an attempt be made to synthesize the inferences drawn and speculations made in the form of a conceptual model. Such a model, taking into consideration geological, hydrological, geochemical and bacteriological attributes of the dynamic system governing the existence of springs in the Anantnag area has been presented in fig 9.1.

The NE-SW section forming the base of the conceptual model, depicts broad lithological and structural characteristics of the area hosting spring discharges. The Valley about 1600 to 1900m above mean sea level which provides the erosional cut necessary to expose the water table to the surface in the form of springs on its either sides, is carved out of an anticlinal structure, which is inferred to have Fenestella Shales and Syringothyris Limestone in its core. Higher altitude regions (> 3000m above mean sea level) are occupied by Punjab Volcanics in the SW and Triassic Limestone in the NE. The Valley is filled up with lacustrine sediments belonging to the Karewa Group and alluvium.

Clearly, as permitted by the geomorphology of the area and consistent with one of the basic tenets of hydrology, most likely regions from where the spring systems could get recharged are higher altitude regions occupied by carbonate rocks and intermediate to basic volcanics. The latter are known to be fractured and jointed rendering them very high permeability in some selected zones. These permeable zones may act as conduits for recharging solutions. In case of carbonate rocks, however, minute fractures developed,
Figure 9.1 Conceptual model showing geochemical and bacterial characteristics.

Ca-Mg-HCO₃ type water with TDS ~ 30 mg/l

Addition of CO₂ as H₂CO₃ in zone of root-respiration and organic decay. Possible oxidation of sulphides, if present and thus addition of SO₄²⁻ to waters.

Dissolution of Mg²⁺ → Ca²⁺

Addition of Cl⁻ through fertilizers

Dissemination of SO₄²⁻ and possibly Cl⁻

Type-D springs

Type-B springs

Type-C springs

Stagnant water

Type-A springs

Dissolution of Ca²⁺, Mg²⁺ and HCO₃⁻

Faecal contaminations from excreta

Karstic features

Possible dissolution of CaSO₄

Possible addition of Na⁺

Addition of Na⁺, Cl⁻ and possibly SO₄²⁻

Panjal

Volcanics

Agglomeratic

Slates

Fenestella

Shales/Syringothyris

Limestone

Attainment of temperature-dependent equilibrium with respect to SiO₂ at depth exceeding 2000m
particularly in the axial portion of the syncline, could have initially facilitated the descent of recharging solutions. Subsequently, these channels must have get enlarged on account of dissolution of carbonates.

It is only logical to infer that recharge waters derived from the precipitation either in the form of snow or rain, are very dilute (TDS \(\approx 30\)) Ca-Mg- HCO\(_3\) type solutions at the inlet end of the hydrological cycle to which they would eventually belong. Some very significant chemical changes occur during the initial stages of the descent when infiltrating solutions come across the weathered zone capping the recharge area. Carbon dioxide, released as a result of root-respiration and through decay of organic matter, gets easily mixed-up with descending solutions resulting in the formation of carbonic acid (H\(_2\) CO\(_3\)):

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3
\]

HCO\(_3^-\) ions added to the solution as carbonic acid dissociates rather readily under the physico-chemical conditions prevailing in the soil zone:

\[
\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-
\]

The addition of H\(^+\) ions through the reaction given above results in lowering the pH of infiltrating solutions thus making them more acidic and consequently more reactive. Continuation of CO\(_2\) addition processes in an open-system may lower the solution pH by up to 0.5 units. Such solution may then be capable of leaching cations from the material they remain in contact with.

It may be speculated that the weathered zone, particularly of Panjal Volcanics, may have some sulphates, generated as a result of in-situ oxidation of primary sulfides.
Such sulphates, on account of their very high solubility in waters, may result in increasing the $\text{SO}_4^{2-}$ content of descending solutions.

For understanding the chemical evaluation of springs of Anantnag area during infiltration of groundwater to still deeper levels, the system hosting them may be considered to consist of two sub-systems which are in hydrological continuity of one another in the central part of the area occupied by the Valley.

The south western sub-system comprises springs discharging from Karewas. These springs are characterized by $\text{Mg}^{2+} > \text{Ca}^{2+}$, $\text{Mg} (\text{HCO}_3)_2 > \text{Ca} (\text{HCO}_3)_2$, relatively high $\text{Cl}^-$ values, lower $\text{HCO}_3^- / \text{Cl}^+ + \text{SO}_4^{2-}$ ratio and high $P\text{CO}_2$. All these characters to these springs have been imparted due to water rock interaction within Punjab Volcanics.

Pyroxene and olivine are more susceptible to chemical alteration processes than plagioclase. Consequently solutions would tend to extract more of $\text{Mg}^{2+}$ than $\text{Ca}^{2+}$. Availability of $\text{HCO}_3^-$ ions would result in forming $\text{Mg} (\text{HCO}_3)_2$ as a more abundant species in the fluid than $\text{Ca} (\text{HCO}_3)_2$. Moreover, basic rocks have relatively high $\text{Cl}^-$ content in the form of $\text{Cl}$ atoms/ $\text{Cl}^-$ ions occurring in intermolecular spaces in uncombined state (Absar et al., 1991) which is readily available to circulating groundwaters. Naturally, therefore, solutions reacting with basic rocks are expected to have higher $\text{Cl}^-$ content than those reacting with carbonate rocks.

High $P\text{CO}_2$ values in Karewa hosted springs, more than 20 times higher than atmospheric $P\text{CO}_2$, tend to indicate lack of chemical reactions resulting in the consumption of $\text{CO}_2$. Most common of these reactions are dissolution of carbonate, $i.e.$,

$$\text{CaCO}_3 + \text{H}_2 \text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$$
and alteration of plagioclase to an assemblage of clay + calcite (Giggenbach, 1981) expressed by the reaction

\[
\text{Plagioclase} + \text{CO}_2 \rightarrow \text{Clay} + \text{Calcite}
\]

Clearly, there is not much of a scope for carbonate-dissolution in Panjal Volcanics. Whatever carbonates may be available to circulating solutions are in the form calcite amygdales and very rarely as veins and veinlets, which naturally may be getting dissolved as solutions are undersaturated to almost same extent with respect to both calcite and dolomite (log SI calcite = log SI dolomite = - 2.2). High $\text{PCO}_2$ and indicated undersaturation with respect to calcite are thus mutually consistent under circumstances of lack of carbonate-dissolution. Dissolved CO$_2$ is evidently not involved in alteration of plagioclase to clay + calcite also. Had this been the case, Karewa springs would have been relatively enriched in their Na and Ca contents. Moreover, indicated oversaturation with respect to carbonates rules out the possibility of the formation of calcite as an alteration mineral.

Before emerging as springs, the solutions must have had flow paths within the Karewas. The possibility that a fraction of their alkali ions are derived from there can not be ruled out. Moreover, there is evidence of dissolution of CaSO$_4$ in these waters as discussed in a preceding chapter. There is likelihood of the occurrence of gypsum/anhydrite in lacustrine Karewa deposits which might have resulted in increasing the $\text{SO}_4^{2-}$ content of these springs.

As for as distribution of trace elements is concerned, an interesting situation is observed with respect to Fe. Karewa springs characteristically have lower Fe values than carbonate hosted springs, a trend contrary to normal expectation in view of the former
having residence within the Panjal Volcanics. This is clearly a case of relative solubility of Fe-bearing carbonates and aluminosilicates. Not much of Fe could be scavenged from the later from within intermediate to basic volcanic rocks due to lack of their susceptibility to chemical alteration reactions.

A point needs to be made here about remarkably uniform distribution of Cr in all the springs sampled. The value, however, is 5 times higher than the recommended upper limit. Clearly Cr values are not lithologically controlled as under such a situation higher values were expected in discharges which during their subsurface residence interacted with Panjal volcanics. As found in a study in Arizona, higher Cr-values may occur within alluvial basins, which may subsequently get redistributed evenly during post-melting flushing.

It needs to be pointed here that the overall chemical evolution of Type-D spring discharges emerging from Karewas has been such that signatures of the meteoric origin of solutions have been obliterated to some extent. The original Ca- Mg-HCO₃ type composition of recharging fluid has been altered to one characterized by Mg(HCO₃)₂ as the dominant solute species and partitioning of Ca⁺⁺ equally with HCO₃⁻ and SO₄⁻. In view of the fact that the solution remains very dilute (TDS< 200 mg/l), these changes may be considered rather drastic.

The north eastern sub-system comprises warm and cold springs discharging either from the carbonate rocks directly or through the alluvium. These springs (Types A, B and C) are inferred to have their recharge zones located within the higher altitude regions occupied by the Triassic Limestone. Their flow paths are also evidently more or less confined to the carbonate rocks. Karst features are common in these rocks clearly
pointing towards the tendency of solutions to dissolve rather than deposit carbonates. This, in turn, implies that the solutions hosted by these rocks are undersaturated with respect to carbonates. Saturation index calculations indicate that Types A, B and C springs are more undersaturated with respect to dolomite (log SI = -3.58 to -2.04) than calcite (log SI = -1.58 to -0.85). The values estimated for $PCO_2$ are relatively constant averaging around 0.006 bars, somewhat lower than the value calculated for Type-D springs. Since carbonate dissolution is the most abundant chemical reaction occurring in the northeastern sub-system (as evidenced by the presence of karstic features and calculated values of SI's), $CO_2$ must have been regularly consumed. In spite of this, $PCO_2$ continues to be 5 to 6 times higher than the atmospheric value. This implies that a constant supply of $CO_2$ is maintained from the soil zone through batches of descending solutions and the system behaves as an open system for all practical purposes.

Both Type-A and Type-B springs are nearly identical in their chemical composition with the general trend of relative abundances of solute species being $Ca(HCO_3)_2 > Mg(HCO_3)_2 > CaSO_4 > NaCl$. Composition of Type-A springs is readily explained through dissolution of carbonates in descending meteoric waters. Type-B springs, compared to those of Type-A are marginally enriched in $Na^+$ and slightly deplete in $Mg^{++}$. These chemical attributes of Type-B springs may be explained by assuming interaction of solutions with clay minerals within the alluvium. While some $Na^+$ may have been added to the solution, $Mg^{++}$ ions may have been adsorbed by some finer clays.

Type-C springs, which are warm and have $SiO_2$ content of 37 to 39 mg/l equivalent to an equilibrium temperature of about 65°C, are clearly the most chemically altered solutions of meteoric origin. The fact that these waters have very high $Na^+$ content
of up to 54mg/l, clearly indicates that these solutions have descended down to levels below the limestone and have interacted with Panjal Volcanics. Relatively high Cl\(^-\) and SO\(_4\)^{-2} content of these waters may also be related to their residence in basic volcanic rocks. For an average geothermal gradient of 30°C/km, temperatures estimated using SiO\(_2\) concentration in these spring discharges, point to the existence of the ‘reaction zone’ at depth exceeding 2km with reference to the recharge level.

Warm springs clearly present a case where chemical signatures of waters having reacted with carbonate rocks have been overprinted by signatures of water-rock interaction in Panjal Volcanics. The result is that water is generated with relative abundances of solute species being NaH CO\(_3\)\(>\) Ca SO\(_4\) \(\approx\) Ca (HCO\(_3\))\(_2\) \(>\) Mg (HCO\(_3\))\(_2\)\(>\) NaCl.

Some chemical changes in spring compositions are related to anthropogenic activities. Concentration levels of SO\(_4\)^{-2} and NO\(_3\)^{-} are clearly influenced by the application of fertilizers within the cultivated field of the valley. The valley, which provides hydrological connection between northeastern and southwestern sub systems, gets flushed during post-melting season. The net result is redistribution of ions related to fertilizers (including Cl\(^-\), as Na Cl may be present in white fertilizers).

All the types of water identified have CaSO\(_4\) as a solute species. It is particularly abundant in warm springs and springs hosted by Karewas. Presence of gypsum within carbonate rocks and lacustrine deposits may, therefore, be not ruled out.

Most significantly, the waters having residence within carbonate rocks are undersaturated with respect to carbonates as inferred from calculated values of saturation index. This situation is analogous to that of springs hosted by Pennsylvania carbonate
rocks. The possibility exists that deeper solutions may have attained equilibrium with respect to carbonates. However, in the final stages of their ascent they mix with near-surface shallow groundwater available in plenty. The mixture thus produced, which eventually discharges as springs, ends up becoming undersaturated with respect to carbonates in its overall chemical behaviour, though the deeper-origin-component present in the mixture may have attained equilibrium with respect to carbonates.

Quantitative differences in spring discharges during pre-melting (winter) and post-melting (summer) seasons are very distant. There is an inverse relationship between the quantity of water discharged at a given spring locality and concentration of major ions in it. During post-melting season spring discharges increase on account of 30 to 40% dilution which gets reflected in apparent lowering of concentration levels of major cations and anions. As a matter of fact, Anantnag area offers a good example of well-documented seasonal variations in discharge quantity and ionic concentration. This, in turn, implies that the springs belong to a very open, hydrologically continuous, dynamic system in which the bulk of the solutions probably take time of the order of few months only to cover the distance between the inlet and the outlet point.

Bacteriological studies have revealed the presence of faecal contaminations in spring waters, often going beyond the limit prescribed. Such contaminations related to human and animal excreta may have their source almost anywhere from hill tops to valleys. Grazing grounds, camps of security forces, settlements, faulty sewage system and stagnant water bodies may all contribute towards faecal contaminations. Relatively fast dispersal of organic contaminations is facilitated by faster movements of groundwaters and annual stirring and flushing of the systems during post-melting season.
The conceptual model presented here by integrating hydrogeochemical and bacteriological characteristics of spring discharges of Anantnag area over a geological base is the first attempt of its kind as far as spring systems of northwestern Himalayas are concerned. This is still a prototype model giving only preliminary information pertaining to chemical evolution of a spring system. The model, however, may be substantially improved by incorporating data on stable and radioactive isotopes, which of course are beyond the scope of this thesis.