

Silica Geothermometry Studies of Shallow Aquifer in Kelantan

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Abstract. The study aimed to analyze the spatial and temporal distribution of silica concentrations in shallow quaternary aquifers across Kelantan, Malaysia. This assessment was crucial for understanding groundwater dynamics, including residence times and potential contamination sources. A total of 32 (29 groundwater and 03 surface water) samples were collected during both pre-monsoon and post-monsoon periods in 2016. Silica concentrations ranged from 6.3 mg/l to 23.4 mg/l pre-monsoon and 6.2 mg/l to 23.5 mg/l post-monsoon. Silica geo-thermometry, based on the chalcedony equation, estimated temperatures ranging from 3.09°C to 37.61°C pre-monsoon and 0.90°C to 37.79°C post-monsoon. Under typical geothermal conditions with an average heat flow of 30°C/km, these temperatures corresponded to depths ranging from 0.02 km to 0.32 km pre-monsoon and 0.01 km to 0.32 km post-monsoon. The shallow depths (less than 0.32 km) indicate relatively rapid groundwater circulation, which aligns with the observed low silica concentrations. These findings suggest minimal anthropogenic influence and short residence times, emphasizing recent meteoric input and surface water inflow as dominant factors shaping water quality in the area.

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1.0 Introduction

Reactions between water and rocks are very important when evaluating the source of anthropogenic effects on the groundwater [1], [2]. The ascending silica content with increasing depth proves that silica has higher values than the groundwater of shallow origin. The silica solubility in groundwater is directly proportional to the temperature [3]. For the study, the ambient temperature of 28 °C is taken as the standard as it was used as the climate zone.

The study was undertaken to gain insights into the extent of groundwater circulation and to examine its characteristics, including residence time and interactions with solid phases, such as the granular zone or bedrock. It is important to note that, while there is a considerable body of literature regarding the relationship between silica and factors like temperature, regional heat flow values, and aquifer depth, silica analysis is not typically included in conventional groundwater studies. [4], [5]. The primary objective of this investigation is to highlight the importance of silica analysis in addressing various groundwater-related concerns in shallow domestic wells.

Numerous silica thermometry equivalences are established over time to estimate the temperature of the sub-surface water circulation. Temperatures assessed by these geothermometers represent the chalcedony and quartz temperature correspondingly. These assumptions lead to the wide dispersion of estimated geothermal temperature when instigating a single geothermometer to all wells in the study [5], [6]. These reasons include vapour phase loss or gain in the reservoir, different fluid composition mixing, and equilibration processes throughout ascension to achieve superfcies as well as the process of dissolution in precipitation. The application of silica geothermometer is pragmatic to over 7000 groundwater samples exhibiting non-thermal characteristics and the results simply indicate that there exists a crucial link between silica geothermometer studies and the regional heat flow. These studies have arrived at relationships that express the equation,

$$\text{Temperature derived from silica from groundwater (T in } ^\circ\text{C)} = mq + b \quad (2.1)$$

The term q signifies regional heat flow in mWm^{-2} , while m and b denote constants using the value and unit of $0.67 \text{ } ^\circ\text{C m}^2 \text{ mW}^{-1}$ and 13.2°C , respectively. In general, the application of quartz geothermometer is applicable in systems involving high-temperature settings ($>150^\circ\text{C}$) contrariwise to the application of chalcedony geothermometer investigation which is often applicable in conditions of lower temperature ($<150^\circ\text{C}$). Based on the explanations, the application that is appropriate concerning groundwater system investigation is the chalcedony geothermometer [4]. The chalcedony geothermometer associated with the solubility of chalcedony can be expressed as follows:

$$t \text{ } ^\circ\text{C} = [(1032)/(4.69 - \log \text{SiO}_2)] - 273.15 \quad (2.2)$$

Based on the equations, $t \text{ } ^\circ\text{C}$ denotes the derived chalcedony temperature of water samples. Converting values of silica concentration into aquifer temperature can provide estimated depth to an aquifer, taking into account the normal geothermal gradient of $30^\circ\text{C}/\text{km}$ and assuming the ambient temperature as well. The estimated depth can be calculated as follows:

$$\text{Estimated depth of aquifer (d in km)} = \frac{t \text{ } ^\circ\text{C} - t_a}{g_g} \quad (2.3)$$

where $t \text{ } ^\circ\text{C}$ denotes the calculated temperature of the calculated chalcedony t_a is the ambient temperature of the atmosphere and g_g is the geothermal gradient constant of $30^\circ\text{C}/\text{km}$. The principal explanation in making this attempt or method is to distinguish aquifer settings or

characteristics of the samples. The major anions chloride (Cl⁻), and fluoride (F⁻) were analyzed using the titration method, and colorimetric method respectively.

3.0 Results and Discussion

3.1 Distribution of Silica

The concentration of silica ranged from 6.3 mg/l to 23.4 mg/l for pre-season and 6.2 mg/l to 23.5 mg/l for post-season (Figure 2). The temperature of samples is calculated using chalcedony Equation (2.2) taking an ambient temperature of 28 °C. The derived chalcedony temperature ranges from 3.09°C to 37.61°C during pre-season and 0.90°C to 37.79°C for post-season, with several samples having negative values as presented in Tables 1. The negative values are due to the very low silica content, so they are not suitable and omitted from the analysis [3], [7]. The positive value of chalcedony temperature derived from the concentration of silica is then applied to calculate the estimated depth of aquifer using the Equation (2.3). The estimated depths to aquifer range from 0.02 km to 0.32 km during pre-season and 0.01 km to 0.32 km for post-season, with the majority of the samples having negative values from the derived values, it can be inferred that the depth of water circulation is limited to shallower depths. The estimates interpreted of aquifer depths are a range of 0.02 km to 0.32 km during pre-season and 0.01 km to 0.32 km for post-season. The silica values are high in the northwest region during pre-season while for post-season high values are observed in the northwest and southeast part with majority concentrations are around between 14 mg/l (Figure 3). This slight enhance in the silica values can be well attributed to the surficial inputs through surface water involvement.

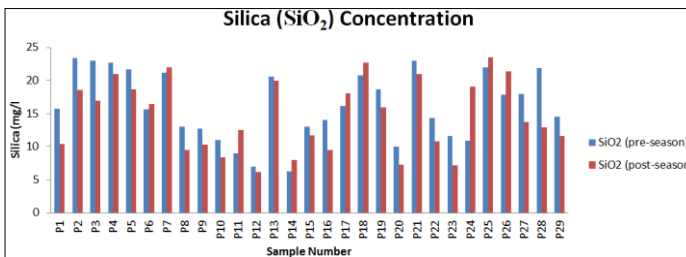


Figure 2: Range of silica concentration in groundwater samples.

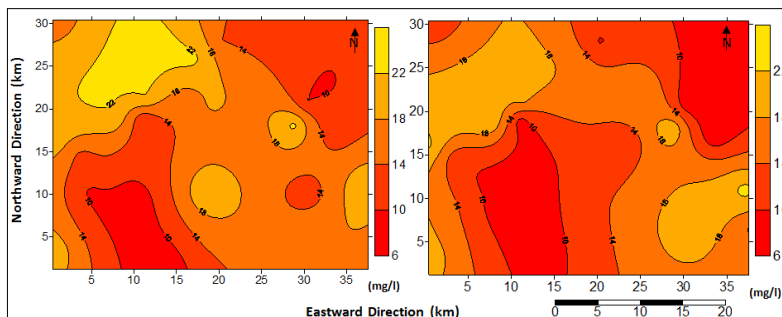


Figure 3: Silica distributions (2D) in groundwater samples during pre-season (left) and post-season (right).

Table 1: Silica values, derived chalcedony temperature and calculated estimated depth of groundwater circulation of groundwater (P) and surface water (S).

| S/No | SiO ₂ (mg/l) Pre-Season | Chalcedony Temperature Pre-Season (°C) | Estimated Groundwater Depth Pre-Season (km) | SiO ₂ (mg/l) Post-Season | Chalcedony Temperature Post-Season (°C) | Estimated GW Depth Post-Season (km) | TDS (mg/l) (Pre season) | TDS(mg/l) (Post season) | Cl ⁻ (mg/l) (Pre season) | Cl ⁻ (mg/l) (Post-Season) |
|------|------------------------------------|--|---|-------------------------------------|---|-------------------------------------|-------------------------|-------------------------|-------------------------------------|--------------------------------------|
| P1 | 15.7 | 22.2 | -0.19 | 10.4 | 7.82 | -0.67 | 75.86 | 126.47 | 47.04 | 39.12 |
| P2 | 23.4 | 37.61 | 0.32 | 18.6 | 28.56 | 0.01 | 87.35 | 116.76 | 41.2 | 65.8 |
| P3 | 23 | 36.92 | 0.29 | 17 | 25.15 | -0.09 | 123.6 | 147.84 | 42.27 | 31.64 |
| P4 | 22.7 | 36.39 | 0.27 | 21 | 33.28 | 0.17 | 275.98 | 195.74 | 45.33 | 62.85 |
| P5 | 21.7 | 34.58 | 0.21 | 18.7 | 28.76 | 0.02 | 265.63 | 241.25 | 31.24 | 25.43 |
| P6 | 15.6 | 21.97 | -0.2 | 16.4 | 23.81 | -0.13 | 196.45 | 138.67 | 21.3 | 27.1 |
| P7 | 21.2 | 33.65 | 0.18 | 22 | 35.13 | 0.23 | 274.59 | 284.34 | 28.4 | 33.6 |
| P8 | 13 | 15.43 | -0.41 | 9.5 | 4.84 | -0.77 | 280.43 | 295.85 | 53.72 | 24.85 |
| P9 | 12.7 | 14.62 | -0.44 | 10.3 | 7.5 | -0.68 | 168.86 | 125.92 | 61.84 | 53.76 |
| P10 | 11 | 9.69 | -0.61 | 8.4 | 0.9 | -0.9 | 163.57 | 138.03 | 45.04 | 39.41 |
| P11 | 9 | 3.09 | -0.83 | 12.5 | 14.06 | -0.46 | 146.97 | 93.48 | 36.38 | 42.75 |
| P12 | 7 | -4.74 | -1.09 | 6.2 | -8.37 | -1.21 | 186.65 | 163.81 | 31.01 | 28.1 |
| P13 | 20.6 | 32.52 | 0.15 | 20 | 31.36 | 0.11 | 257.85 | 218.45 | 42.76 | 39.6 |
| P14 | 6.3 | -7.89 | -1.19 | 8 | -0.63 | -0.95 | 157.97 | 183.39 | 24.52 | 47.25 |
| P15 | 13 | 15.43 | -0.41 | 11.7 | 11.79 | -0.54 | 156.76 | 129.71 | 24.63 | 31.86 |
| P16 | 14 | 18.05 | -0.33 | 9.5 | 4.84 | -0.77 | 143.76 | 104.46 | 18.4 | 26.4 |

| | | | | | | | | | | |
|------------|------|-------|-------|------|-------|-------|--------|--------|-------|-------|
| P17 | 16.1 | 23.13 | -0.16 | 18.1 | 27.52 | -0.01 | 297.86 | 250.92 | 23 | 39.6 |
| P18 | 20.8 | 32.9 | 0.16 | 22.7 | 36.39 | 0.27 | 304.35 | 273.39 | 42.56 | 31.47 |
| P19 | 18.7 | 28.76 | 0.02 | 15.9 | 22.67 | -0.17 | 296.54 | 294.29 | 50.05 | 46.25 |
| P20 | 10 | 6.52 | -0.71 | 7.3 | -3.46 | -1.04 | 73.34 | 61.03 | 43.14 | 40.87 |
| P21 | 23 | 36.92 | 0.29 | 21 | 33.28 | 0.17 | 284.37 | 273.74 | 32.59 | 21.06 |
| P22 | 14.3 | 18.81 | -0.3 | 10.8 | 9.08 | -0.63 | 143.49 | 116.69 | 39.45 | 24.63 |
| P23 | 11.6 | 11.49 | -0.55 | 7.2 | -3.88 | -1.06 | 99.38 | 126.54 | 38.34 | 32.57 |
| P24 | 10.9 | 9.39 | -0.62 | 19.1 | 29.58 | 0.05 | 197.75 | 154.63 | 20.27 | 23.82 |
| P25 | 22 | 35.13 | 0.23 | 23.5 | 37.79 | 0.32 | 193.45 | 167.77 | 52.54 | 44.3 |
| P26 | 17.9 | 27.09 | -0.03 | 21.4 | 34.03 | 0.2 | 214.45 | 189.45 | 42.6 | 35.17 |
| P27 | 18 | 27.31 | -0.02 | 13.7 | 17.28 | -0.35 | 267.45 | 245.03 | 32.57 | 21.32 |
| P28 | 21.9 | 34.95 | 0.23 | 12.9 | 15.16 | -0.42 | 187.87 | 133.28 | 29.46 | 22.08 |
| P29 | 14.5 | 19.31 | -0.28 | 11.6 | 11.49 | -0.55 | 96.56 | 63.91 | 27.95 | 36.67 |
| S1 | 15.3 | 21.26 | -0.22 | 12.5 | 14.06 | -0.46 | 74.74 | 83.52 | 32.62 | 17.42 |
| S2 | 17.8 | 26.88 | -0.03 | 14.6 | 19.56 | -0.28 | 178.76 | 194.59 | 31.1 | 23.51 |
| S3 | 21.8 | 34.76 | 0.22 | 16.5 | 24.04 | -0.13 | 50.39 | 83.78 | 26.04 | 17.45 |

3.2 Chloride, (Cl⁻) against Silica Content

Generally, chloride is an inert component in natural conditions involving rock water surroundings [8]. Chloride remains uninterrupted both at elevated temperatures and ambient temperatures when in a solution [9]. Chloride is not easily absorbed on mineral surfaces and also does not react with common rock-forming minerals owing to its huge ion size [10], [11]. Attributing to the explanations, the concentration of silica is interrelated to chloride to appraise the role of anthropogenic conditions and natural impacts on ion acquisition. For pre-season, 4 significant clusters can be observed in SiO₂-Cl plot from Figure 4. Locations P12 and P14 form a cluster. Secondly, locations P11, P20, P24, P10, P23, P29, P9, P8, P1, P22, S1, P15, P16, P6 and P17 form another cluster. These samples exhibit a good positive correlation which denotes increasing silica content relative to chloride. Location points P19, P26, P27 and S2 form another cluster while locations P25, P13, P3, P4, P2, P5, P7, S3, P28 and P21 form the other cluster suggesting low to normal SiO₂-Cl relationship which could offer typical normal role of water-rock interaction since the higher position of these cluster in the plot. This cluster which lies straight up hardly shows any change in silica concentrations around 6 mg/l to 24 mg/l. Chloride concentrations shown by these sub-clusters are between 18 mg/l and 62 mg/l. Although chloride concentrations are well below the desirable limits, the correlated silica values for the same samples depict that chloride is being contributed to the groundwater system via processes other than rock-water interactions attributed to the acquisition of SiO₂. Here one noteworthy point is that the majority of the samples show low silica values which are lesser than normal silica values and thus could have a reduced impact on the groundwater system. The only possible explanation could be that these waters are of very recent origin such as from meteoric sources.

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Samples P12 and P14 form a cluster that is less significant, making it clearer that rock-water interaction is there but its role in ion acquisition is very minimal. Thus, silica thermometry is not appropriate for samples P12 and P14 as the silica concentration of these samples is far too minor than the concentrations routinely extracted from the groundwater. These values are pertinent to distinguish surface or stream water compared to groundwater. The majority of these samples have lower silica values corresponding to the chloride values. Hence, the rise in silica values is not associated with any drastic change in chloride ion values which clues that rock-water interaction is not controlling chloride in groundwater.

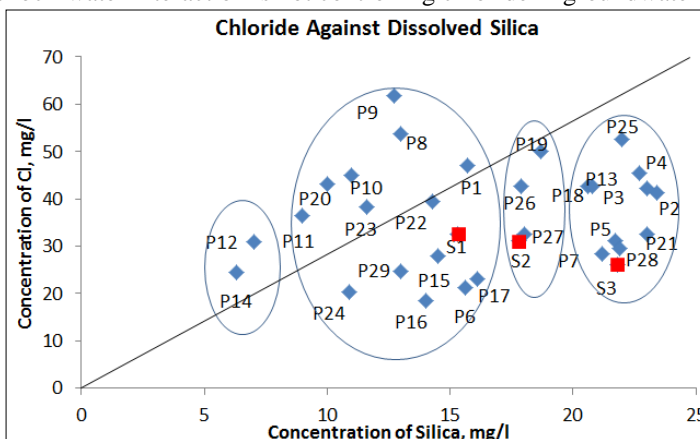


Figure 4: Chloride against silica in groundwater (blue) and surface water (red) during pre-season.

For post-season, 2 clusters can be observed in SiO_2 -Cl plot as shown in Figure 5. Locations P12, P23, P20, P14, P9, P1, P11, P10, P29, P16, P22, P15, P8, P28, S1, P27 and S2 form a cluster while location P19, P17, P3, P6, S3, P2, P4, P13, P5, P24, P26, P21, P7, P18 and P25 form another cluster. In addition, from a chloride point of view, P2 and P4 can also be horizontally grouped into a cluster. Both clusters show silica variation into two groups ranging between 5 mg/l to 15 mg/l while another cluster shows variation from 15 mg/l to 24 mg/l. For the post-season, there are two clusters compared to the pre-season which is four. The silica values in the study area have lower variations compared to pre-season. Although chloride concentrations are low with the highest of 65.8 mg/l, less than the standard of 250 mg/l, chloride ion is contributed in groundwater systems via processes other than rock water interaction. This is because the values of silica derived are in low concentrations indicating that SiO_2 has a low impact in the groundwater system. Some of the plots show constant silica values with varying chloride values. Based on these characteristics, it can be inferred that groundwater samples with low silica concentrations indicate less water-rock contact with shorter residence time [7].

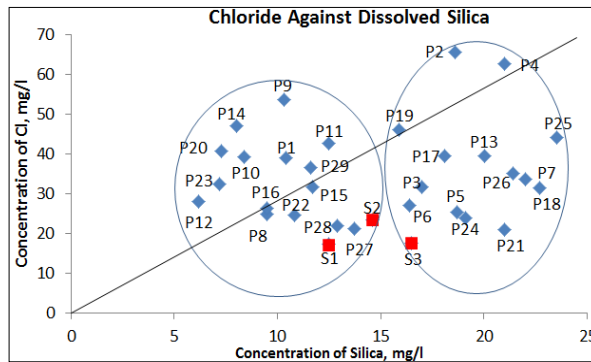


Figure 5: Chloride against silica in groundwater (blue) and surface water (red) during post-season.

3.3 TDS against Silica Content

From the SiO_2 -TDS plot (Figure 6), groundwater samples during pre-season demonstrate an increasing trend based on SiO_2 -TDS relationship. The groundwater samples show an increasing trend of silica values with marginal change in TDS values, indicating constituents of natural sources, with little anthropogenic source. Locations P4, P5, P7, P13, P18 and P21 form a cluster with TDS ranging from 250 mg/l to 305 mg/l. From the tabulated data, it can be observed that low silica values (< 30 mg/l) tend to occur in regions with higher TDS concentrations. This indicates that samples with high TDS concentration have a substantial component of a low quantity of groundwater of deeper origin. The low silica values indicate low residence time for the groundwater body in the aquifer.

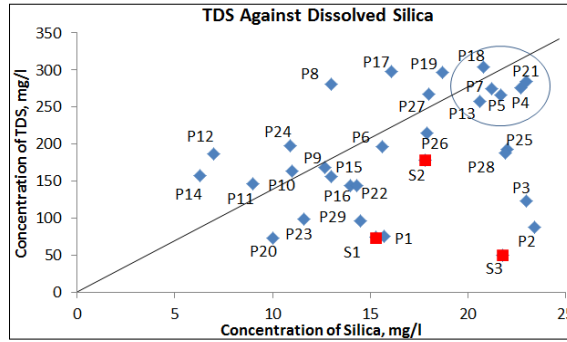


Figure 6: TDS against silica in groundwater (blue) and surface water (red) during pre-season.

Based on the SiO_2 -TDS plot of samples collected during post-season, all samples show a normal SiO_2 -TDS relationship (Figure 7). This indicates rock water interaction, but its role is limited only up to the acquisition of silica values and is not associated with any drastic rise in TDS values. The normal relationship also reflects the smoothening of the Silica-TDS relationship line due to the inflow of rainwater of low silica values than groundwater. Figure 7 shows samples that fall in 3 vertical clusters. Location P8, P12, P14, P10, P23, P20, P9, P16, P1, P22, P15, P28, P11, S1, P29, S2 and P27 form one cluster. Locations P19, P3, P6 and S3 form another cluster while location P2, P24, P25, P26, P4, P13, P5, P17, P7, P18 and P21 form the third cluster. All these clusters show a linkage of constant silica values with varying TDS concentrations, which again makes it clear that most of the ion acquisition is taking place through interactions other than those accountable for silica acquisition.

Silica concentrations in surface runoff are poorer throughout periods of high precipitation or monsoon season and higher during drier months relative to groundwater. The nature of surface water bodies indicates low silica content which generally indicates shallower water sources. Hence, during the drier period, the main source of inflow into the river is from groundwater located in the aquifer. On the other hand, an elevated amount of silica precipitation occurs which becomes diluted and decreases in the river during heavy storms. In groundwater, the average silica concentration is 17 mg/l while for surface water is 14 mg/l. On these bases, the groundwater and surface water contain low silica content with minor variations between the bodies thus concluding possible identical origins of water from shallow origins. Since the values of silica are quite low, less than 25 mg/l, the role of silica acquisitions in groundwater attributed to TDS content can be negligible [12]

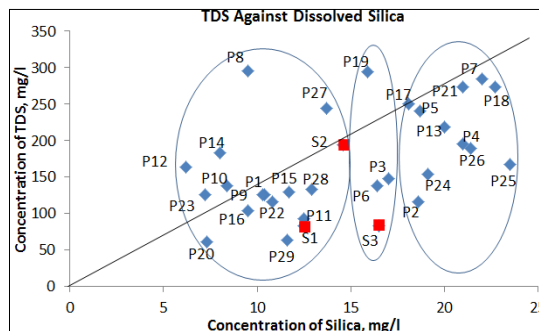


Figure 7: TDS against silica in groundwater (blue) and surface water (red) during post-season.

4.0 Conclusion

The present investigation shows that SiO₂ values are very vital while assessing the depth of groundwater circulations, the evolution of groundwater chemistry through various hydrogeochemical processes, and geogenic or anthropogenic involvement that may influence the distribution of major ions in groundwater.

Based on silica geothermometry the groundwater circulation depth during the pre-season ranges from 0.02 km to 0.32 km while for the post-season, the circulation depths fluctuate between 0.01 km and 0.32 km. The chloride values fall well below the desirable limits, but the varying chloride values with constant silica values point to the negligible rock water interaction in the area. The silica-TDS relationship indicates that role of rock-water interaction is not substantial as far as the ion acquisition is concerned.

Such low Silica levels reflect minimal involvement of anthropogenic activities and small residence time of groundwater in terms of rock-water interaction. These low silica values also show that the water in the area is of recent meteoric origin.

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References

1. Z. Mamat, U. Halik, P. Muhtar, I. Nurmatamat, and A. Abliz, "Temporal variation of significant soil hydrological parameters in the Yutian oasis in Northwest China from 2001 to 2010," *Environ. Earth Sci.*, vol. **75**, 1–16 (2016).
2. N. Rahmawati, J.-F. Vuillaume, and I. L. S. Purnama, "Salt intrusion in Coastal and Lowland areas of Semarang City," *J. Hydrol.*, vol. **494**, 146–159 (2013).
3. A. B. Carlson and C. V Banks, "Spectrophotometric determination of silicon," *Anal. Chem.*, **24** (3), 472–477 (1952).
4. W. Robert and I. I. Potter, "A revised and expanded silica (quartz) geothermometer," *Bull. Geotherm. Resour. Counc.*, **11**, 3–12, (1982).
5. A. Khan, R. Umar, and H. H. Khan, "Significance of silica in identifying the processes affecting groundwater chemistry in parts of Kali watershed, Central Ganga Plain, India," *Appl. Water Sci.*, **5**, pp. 65–72, (2015).
6. M. M. A. Khan and R. Umar, "Significance of silica analysis in groundwater in parts of Central Ganga Plain, Uttar Pradesh, India," *Curr. Sci.*, **98** (9), 1237–1240 (2010).
7. A. M. Shapiro, "Cautions and suggestions for geochemical sampling in fractured rock," *Groundw. Monit. Remediat.*, **22** (3), 151–164 (2002).
8. N. J. Raju, P. Patel, D. Gurung, P. Ram, W. Gossel, and P. Wycisk, "Geochemical assessment of groundwater quality in the Dun valley of central Nepal using chemometric method and geochemical modeling," *Groundw. Sustain. Dev.*, **1**, pp. 135–145 (2015).
9. A. J. Ellis, "Quantitative interpretation of chemical characteristics of hydrothermal systems," *Geothermics*, **2**, 516–528 (1970).
10. M. Vasanthavignar *et al.*, "Application of water quality index for groundwater quality assessment: Thirumanimuttar sub-basin, Tamilnadu, India," *Environ. Monit. Assess.*, vol. **171**, 595–609 (2010).
11. L. F. Yee, M. P. Abdullah, S. Ata, A. Abdullah, B. Ishak, and K. Nidzham, "Chlorination and chloramines formation," *Malaysian J Anal Sci*, **12** (3), pp. 528–535, (2008).

12. S. N. Davis, “Silica in streams and ground water,” *American Journal of Science*, vol. **262**, no. 7. pp. 870–891 (1964).