Study of Hydrogeochemical and Geochemical Properties of Surface Water (Case Study: Comparison of two Adjacent Catchments, Cheshmeh Kileh and Shiroud, Northern Iran)

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Abstract

Cheshmeh Kileh and Shiroud are among the most important rivers of western Mazandaran Province (northern Iran). Sampling sites were determined based on the design of the DEM and geogenic and anthropogenic effects, and water and sediment samples were collected in September 2021. Hydrogeochemical and qualitative diagrams of irrigation were drawn based on the laboratory reported values. The heavy metals, irrigation and industrial indices were calculated for water samples and heavy metals indices were calculated for sediments. Also, dendrograms were drawn to evaluate heavy metals in water and sediment. The results showed that the amount of calcium and sulfate ions at the source of Seh-Hezar sub-river was higher than other samples in this sub-river, which is caused by the dissolution of gypsum in the structure of the Karaj Formation located in Maraan upstream. In Cheshmeh Kileh Catchment, one of the samples had a higher amount of bicarbonate, sodium, potassium and heavy metals ions than other samples due to the infiltration of landfill waste water. The hydrogeochemical diagrams for Shiroud Catchment showed that in the estuary, the phenomenon of saltwater infiltration has occurred due to excessive sand and gravel harvesting. Given industrial quality indices, some samples have sedimentation properties and some have corrosion properties. Accordingly, when using surface water in this region for industrial activities, further case studies are needed. The quality of irrigation water at some stations was unsuitable for agricultural activities in some indices. Also, the statistical charts show scatters in the samples of the source and landfill leachate.

1 Introduction

Water is an essential asset and an important national resource that forms the basic components of the biological system [1]. Over the past few decades, there has been an increasing demand for water resources. Industrial growth, population growth and other development activities have not only led to increasing demand for water, but also caused a reduction in quality, which exacerbates water crisis [2]. Tharmar et al. 2022 believed that rivers can provide fresh water for various domestic, agricultural and industrial uses. River ecosystems play an important role in regulating the environment, transporting nutrients, absorbing urban and industrial waste, and controlling flood and drought. Many of these functions are inextricably linked to river health indices such as water quality, ecological status, and flow [3].

Geochemical conditions have a significant effect on surface water quality. Hydrogeochemical studies explain the relationship between water chemistry and aquifer lithology for water quality. Such a relationship not only helps to explain the origin and distribution of dissolved components, but also helps to clarify the controlling factors of surface water chemistry [4]. The most susceptible water resources against pollution are rivers because they carry a large amount of industrial and urban wastewater along with chemical fertilizers in the form of runoff from agricultural lands [4, 5, 6].

Safari et al. 2020 in a study investigated the hydrogeochemical properties and water quality of the Aji-Chay River, east Urmia Lake, and described the effects of geological formations on the evolutionary process of this river. According to the results, the samples in Aji-Chay River upstream have calcium bicarbonate type and in the downstream due to the influence of the lithology of the formations such as the dissolution of halite minerals and the increase in sodium and chlorine ions, the water type changes to sodium chloride [7]. Also, Richards et al. 2022 on the hydrogeochemical dynamics of the Ganges River, India found that factors such as dilution, evaporation, water-rock interactions (including carbonate and silicate weathering) and human inputs are among the main determinant of the water chemistry of the Ganges River [8]. In a study, Fang et al. 2022 studied the surface sediments of the Nanfei River for the human effect on the distribution and bioavailability of heavy metals. The results showed that cadmium showed the highest enrichment in river sediments, indicating massive pollution caused by human activities [9].

In this study, the hydrogeochemistry and heavy metals of water and sediment in the Cheshmeh Kileh and Shiroud Catchments were investigated. The Cheshmeh Kileh and Shiroud are adjacent rivers and the most important rivers in western Mazandaran Province, northern Iran, passing through mountainous, forest, and agricultural lands and residential areas and ending at the Caspian Sea.

Both rivers in southern Caspian Sea have are very important as habitats for the migration and reproduction of valuable fishery species such as salmon (Salmo Trutta Caspius) and white fish (Rutilus Frisii Kutum) [10]. Therefore, conducting comprehensive studies to determine factors affecting the chemical composition of water and the process of quality changes in surface water and sediment along the rivers can help to identify pollutants and controlling factors of water chemistry and the sustainable development of the region. The objective of this study was to compare the hydrogeochemical and geochemical properties of Shiroud and Cheshmeh Kileh rivers and investigate the origin and difference of pollutants in these catchments.

The study area is located between 36° 19' 20" and 36° 53' 00" N latitudes and 50° 30' 00" and 50° 58' 16" E longitudes (Fig. 1). The Cheshmeh Kileh has two sub-rivers of Do-Hezar and Seh-Hezar, the Do-Hezar originates from the heights of Nosha and northern Alamut, and the Seh-Hezar originates from the Alam-Kuh peak glacier. The Shiroud River also originates from Balaband, Pishkoh and Dimron mountains, and it is formed by the joining of two sub-rivers, Tirom Roud and Pastangar Roud. According to the report of the synoptic station in western Mazandaran Province, the type of climate is humid with hot summers and slightly cold winters.

2 Geology of the study area

According to the classification of Guest et al. 2006 [11, 12] in terms of geological structures, the study area is located in the central Alborz zone and in the northern Alborz subzone. The general direction of the geological structures of the region is northwest-southeast and they were created by a lot of faults (thrust type) and folds. The density of fault and fold systems have caused a height difference of more than 4000m in a relatively short distance (about 25 km). According to the report of the Geological Survey and Mineral Exploration of Iran (GSI), Karaj, Tizkuh, Shemshak, Elika, Ruteh, Nesen, Dorud, Mobarak, Mila formations, equivalent units of Lalun and Kahar, Zaigun, Barut and Soltanieh dolomite (since the Precambrian to the Quaternary) have been reported in the Cheshmeh Kileh Catchment. Mineral deposits of pyrite, barite, copper, zinc, coal, conglomerate, silica and iron have been recorded in this catchment [13, 14] (Fig. 2). Also, there are 3 active sand mines in Seh-Hezar sub-river and 2 active sand mines in the main river (Cheshmeh Kileh). Also, the landfill of Tonekabon and Shiroud cities is located in this catchment, the wastewater of which after traveling through Hyrcanian forests and finally flows into Cheshmeh Kileh river. Dorud, Mobarak and Ruteh formations have also been reported in the Shiroud Catchment [13] (Fig. 3). There are also 3 active sand mines in the river downstream.

3 Methods

In order to sample of the canals and rivers and sub-rivers of the study area, first, the dividing line of Cheshmeh Kileh and Shiroud Catchments was determined. Then, by the DEM map, the canals were graded by Strahler method and the center of gravity of the catchment was determined. Based on the grade of the canals as well as the location of possible anthropogenic and geogenic pollution points, points were added to the sampling network and thus 23 stations for the Cheshmeh Kileh Catchment and 14 stations for the Shiroud Catchment were selected for sampling (Fig. 5). However, at the time of sampling, given that it is difficult to pass and the lack of access to some points, as well as the fact that the area is difficult to pass during the rainy season and high discharge, sampling was only done in September 2021 in low rain season and a total of 20 stations for Cheshmeh Kileh and 12 stations for Shiroud were sampled. Stations CH1-CH8 in Seh-Hezar sub-river (including dominant sedimentary lithology), stations CH12-CH15 in Do-Hezar sub-river (including dominant sedimentary and igneous lithology) and stations CH16-CH23 in the river of Cheshmeh Kileh have been sampled. Also, stations SH3-SH14 in the Shiroud Catchment were sampled. Two water samples and one sediment sample were taken from each station.

Polyethylene containers were used to sample flowing water in the bed of canals and rivers. For this purpose, a polyethylene bottle was used to measure cations and a polyethylene bottle to measure anions and other chemical parameters. At each station, before sampling, the sampling bottle was washed three times with the river water sample. The samples related to the measurement of cations at the sampling site were passed through a 45 micron filter based on the American Public Health Association (APHA) standard and laboratory instructions, and then the acidity was reduced to less than 2 using 65% nitric acid [8, 15]. The samples were transferred to Zarazma Minerals Studies Company (Tehran, Iran) at an interval of 24 hours after sampling, and ICP-MMS, nitrate, sulfate, carbonate, bicarbonate, chloride, acidity (pH), total dissolved solids (TDS) tests, electrical conductivity (EC) and alkalinity tests were performed on the sent samples.

Sediment samples were collected from fine-grained sediments deposited in the active bed of the river by a plastic shovel and kept in a plastic bag and labeled. In the laboratory of Zarazma Minerals Studies Company, the samples were first dried in a laboratory oven at a maximum temperature of 100 °C. After crushing, splitting and pulverizing, the samples were passed through a 200 mesh (75 micron) sieve. Then, the samples were digested by dissolving 4 acids (HF/Multi Acid Digest). Finally, the samples were read using ICP-MMS and the amount of heavy metals were determined.

According to the laboratory results, by Rockware AqQA 10.5.0, Piper, Stiff and Ternary diagrams and Gibbs diagram were drawn by Microsoft Excel Worksheet for hydrogeochemical comparison and determining the mechanism controlling the chemical composition of water in both catchments. Using Excel, Wilcox and USSL diagrams were drawn to evaluate the ability of river water to be used for agriculture. Then, the quality indices of irrigation and industry and the indices of heavy metals in water were calculated and classified (Tables 1, 2, 3). Next, dendrogram diagrams for heavy metals in sediment and water were drawn by IBM SPSS Statistics 27, and the relationship between heavy metals in water and sediment and the distribution of data in both catchments were investigated. Finally, all figures have been output using Corel Draw software for easier interpretation and comparison.

Table 1
Classification of industrial quality indices and calculation methods[16].

References	Equation	Classification	Index value	Index
[17, 18]	$\mathrm{LSI} = \mathrm{pH}\text{-}\mathrm{pH_s}$ $\mathrm{pH_s} = (9.3+\mathrm{A}+\mathrm{B})\text{-}(\mathrm{C}+\mathrm{D})$ $\mathrm{A}=(\log_{10}[\mathrm{TDS}]\text{-}1)/10$ $\mathrm{B}=\text{-}13.12\times\log_{10}\left(°\mathrm{C}+273\right)+34.55$ $\mathrm{C}=\log_{10}\left[\mathrm{Ca^{2+} as\ CaCO_3}\right]\text{-}0.4$ $\mathrm{D}=\log_{10}[\mathrm{Alkalinity\ as CO_3}]$	Water is supersaturated with respect to $CaCO_3$	LSI > 0	Langelier Saturation Index
		Water is considered to be neutral	LSI = 0	
		Water is undersaturated with respect to $CaCO_3$	LSI < 0	
[19]	$\mathrm{RSI} = 2\left(\mathrm{pH_s}\right) - \mathrm{pH}$	Water is supersaturated with respect to $CaCO_3$	RSI < 6	Ryzner Saturation Index
		Water is considered to be neutral	6 < RSI < 7	
		Water is undersaturated with respect to $CaCO_3$	RSI > 7	
[19]	$\mathrm{PSI}=2\left(\mathrm{pH_s}\right)\text{-}\mathrm{pH_{eq}}$	Water has a tendency to encrust	PSI < 4.5	Puckorius Scaling Index
		Water is considered to be neutral	$4.5 \le$ PSI $\le$ 6.5	
		Water has a tendency to corrosion	PSI > 6.5	
[17]	$\mathrm{CR}=\frac{\left[\frac{\mathrm{Cl^-}}{35.5}+2\left(\frac{\mathrm{SO_4^{2-}}}{96}\right)\right]}{\left[2\left(\frac{\mathrm{HCO_3^-}+\mathrm{CO_3^{2-}}}{100}\right)\right]}$	Water transfer is permitted by any type of pipe	CR < 1	Corrosion Ratio
		Water transfer by metal pipe is not allowed	CR > 1	
[20]	$\mathrm{LS}=\frac{\mathrm{epm\ Cl^-}+\mathrm{epm\ SO_4^{2-}}}{\mathrm{epm\ HCO_3^-}+\mathrm{epm\ CO_3^{2-}}}$	Water does not have a corrosive character	LSI < 0.8	Larson-Skold Index
		Water has a tendency to corrosion	0.8 < LSI < 1.2	
		Water is highly corrosive	LSI > 1.2	

Table 2
Classification of irrigation quality indices and calculation methods [21].

References	Equation	Classification	Index value	Index
[22]	Obtained from the laboratory method	Excellent	< 250 (µS/cm)	Electrical Conductivity (EC)
		Good	250–750	
		Permissible	750–2250	
		Doubtful	2250–5000	
		Unsuitable	> 5000	
[23]	Obtained from the laboratory method	Freshwater	0-1000 mg/l	Total Dissolved Solids (TDS)
[24]	$TH(CaCO_3) = 2.497Ca^{2+} + 4.11Mg^{2+}$	Soft	0-75mg/l	Total Hardness (TH)
		Moderately hard	75-150mg/l	
		Hard	150–300 mg/l	
		So hard	> 300mg/l	
[25]	$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}}$	Suitable	< 1	Kelly’s Ratio (KR)
		Excess level	> 1	
[26]	$SSP(Na\%) = \frac{Na^{+} + K^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \times 100$	Excellent	< 20	Soluble Sodium Percentage (SSP)
		Good	20–40	
		Fair/Permissible	40–80	
		Poor	> 80	
[21, 27]	$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$	Excellent	< 10 mg/l	Sodium Adsorption Ratio (SAR)
		Good	10–18 mg/l	
		Doubtful	18–26 mg/l	
		Unsuitable	> 26 mg/l	
[28]	$RSC = (HCO_3^{-} + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$	Good	< 1.25 meq/l	Residual Sodium Carbonate (RSC)
		Fair	1.25–2.5 meq/l	
		Weak - Unsuitable	> 2.5 meq/l	
[29]	$RSBC = HCO_3^{-} - Ca^{2+}$	Safe	< 5 meq/l	Residual Sodium Bi-Carbonate (RSBC)
		Marginal	5–10 meq/l	
		Unsatisfactory	> 10 meq/l	
[24]	$MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100$	Excellent	< 50	Magnesium Hazard (MH)
		Harmful for soil	> 50	
[30]	$PI = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{Ca^{2+} + Mg^{2+} + Na^{+}} \times 100$	Good for Irrigation	> 75%	Permeability Index (PI)
		Unsuitable for Irrigation	< 25%	
[31]	$PS = Cl^{-} + \frac{1}{2}SO_4^{2-}$	Suitable	< 3	Salinity Potential (PS)
		Unsuitable	> 3	

Table 3
Classification of heavy metals indices and calculation methods.

References	Equation	Classification	Index value	Index	
[32]	$C_d = \sum Cf_i$ $Cf_i = \frac{M_i}{MAC_i}$	low	$C_d < 1$	**Degree of contamination (C_d)**	Water
		moderate	$1 < C_d < 3$		
		high pollution	$C_d > 3$		
[32, 33]	$HEI = \sum_{i=1}^{N} \left(\frac{C_i}{MAC_i}\right)$	Low pollution	HEI < 10	**Heavy Metal Evaluation index (HEI)**	
		Moderate	10 < HEI < 20		
		High pollution	HEI > 20		
[34, 35]	$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right)$	uncontaminated	$I_{geo} < 0$	**Geological Accumulation Index (I_{geo})**	Sediment
		uncontaminated to moderately contaminated	$0 < I_{geo} < 1$		
		moderately contaminated	$1 < I_{geo} < 2$		
		moderately to strongly contaminated	$2 < I_{geo} < 3$		
		strongly contaminated	$3 < I_{geo} < 4$		
		strongly to extremely contaminated	$4 < I_{geo} < 5$		
		extremely contaminated	$I_{geo} \geq 5$		
[36, 37]	$EF = \frac{HM_s / HM_b}{Fe_s / Fe_b}$	no enrichment	EF < 1	**Enrichment factor (EF)***	
		less enrichment	1 ≤ EF < 3		
		moderate enrichment	3 ≤ EF < 5		
		moderately high enrichment	5 ≤ EF < 10		
		high enrichment	10 ≤ EF < 25		
		very high enrichment	25 ≤ EF < 50		
		exceptionally high enrichment	EF > 50		
[37]	$CF = \frac{HM_s}{HM_b}$	low contamination	CF < 1	**Contamination factor (CF)**	
		moderate contamination	1 < CF > 3		
		high contamination	3 < CF > 6		
		very high contamination	CF > 6		

* Fe_s and Fe_b are the sample and background Fe concentrations, respectively.

4 Discussion and Results

4.1 Controlling mechanism and hydrogeochemical evaluation

Table 4 shows the results of laboratory analysis in the form of descriptive statistics.

Table 4
The results of laboratory analysis in the form of descriptive statistics.

Catchment	Sample	Parameters	Units	Average	Maximum	Minimum	Standard deviation	Median
Shiroud	**Water**	SO_4^{2-}	mg/l	93.60	785.75	13.12	218.20	35.915
		NO_3^-	ppm	4.6	6	1.78	1.23	5.02
		Alkalinity	ppm	184.75	213	153	19.26	181.5
		pH	-	8.5	8.89	7.95	0.32	8.525
		EC	µS	831.66	5790	313	1561.90	380.5
		TDS	ppm	609.47	4632	200.32	1266.99	243.52
		Cl^-	ppm	261.42	2707	30	770.19	38
		CO_3^{2-}	ppm	8.58	20	0	8.19	9.5
		HCO_3^-	ppm	245	316	151	50.50	250.5
		Al	mg/l	0.03	0.04	0.02	0.00603	0.03
		As	µg/l	-	-	< 1	-	-
		Ba	µg/l	49.15	80.9	17.66	15.66	49.14
		Ca	mg/l	56.75	67.19	44.84	6.99	56.33
		Cd	µg/l	-	-	< 1	-	-
		Cr	µg/l	12.81	15.48	9.81	1.93	13.175
		Cu	µg/l	-	-	< 1	-	-
		Fe	mg/l	0.005	0.03	< 0.01	0.009045	0.01
		K	mg/l	2.015	2.85	1.07	0.46	2.03
		Mg	mg/l	18.37	27.48	13.04	3.83	17.355
		Mn	mg/l	-	-	< 0.01	-	-
		Mo	µg/l	0.745	1.82	< 1	0.81	0.515
		Na	mg/l	8.90	22.39	4.39	4.73	9.05
		Ni	µg/l	-	-	< 1	-	-
		Pb	µg/l	-	-	< 1	-	-
		Sb	µg/l	-	-	< 1	-	-
		Se	µg/l	1.07	4.23	< 1	1.64	1
		V	µg/l	-	-	< 1	-	-
		Zn	µg/l	-	-	< 1	-	-
	Sediment	Cd	ppm	0.16	0.3	0	0.11	0.15
		Cr	ppm	88.08	117	63	17.18	88.5
		Cu	ppm	32.25	63	19	14.42	25.5
		Fe	ppm	45175.25	56420	32695	6155.274	46506
		Ni	ppm	38.25	48	24	7.42	40
		Pb	ppm	9.25	22	2	6.8	8
		V	ppm	112.33	146	88	20.21	109.5

Catchment	Sample	Parameters	Units	Average	Maximum	Minimum	Standard deviation	Median
		Zn	ppm	83.66	108	55	15.62	85
Cheshmeh Kileh	Water	SO_4^{2-}	mg/l	73.38	410.86	10.2	85.87	55.97
		NO_3^-	ppm	3.18	6.2	0.77	1.26	3.12
		Alkalinity	ppm	224.4	1575	90	318.99	160
		pH	-	8.4	8.88	7.84	0.32	8.45
		EC	µS	590	3940	324	796	405
		TDS	ppm	411	3152	207	650	259
		Cl^-	ppm	53.55	211	38	37.46	45
		CO_3^{2-}	ppm	20.85	78	0	18.2	20
		HCO_3^-	ppm	402.05	4148	117	883.35	217
		Al	mg/l	0.0525	0.2	0.02	0.04	0.04
		As	µg/l	12.29	34.07	1.34	18.86	1.47
		Ba	µg/l	19.91	40.01	8.68	7.44	17.66
		Ca	mg/l	73.46	208.48	53.64	32.87	69.39
		Cd	µg/l	-	-	< 1	-	-
		Cr	µg/l	18.44	131.9	3.8	27.93	12.39
		Cu	µg/l	-	-	< 1	-	-
		Fe	mg/l	0.104	0.43	0.01	0.18	0.03
		K	mg/l	18.06	323.7	0.8	71.95	1.915
		Mg	mg/l	16.77	40.31	9.25	6.21	16.07
		Mn	mg/l	0.085	0.16	0.01	0.11	0.085
		Mo	µg/l	3.04	7.59	1.11	1.55	2.75
		Na	mg/l	24.94	313.4	3.3	68.08	10.415
		Ni	µg/l	21.405	41.06	1.75	27.8	21.405
		Pb	µg/l	4.055	4.76	3.35	0.997	4.055
		Sb	µg/l	-	-	< 1	-	-
		Se	µg/l	2.17	3.46	1.53	0.58	2.015
		V	µg/l	10.32	10.32	< 1	-	10.32
		Zn	µg/l	3.34	14.55	1.04	4.61	1.5
	Sediment	Cd	ppm	0.28	0.6	0.1	0.14	0.3
		Cr	ppm	52.1	132	34	22.24	45
		Cu	ppm	27.6	69	16	13.41	23
		Fe	ppm	27759.3	50017	20792	6431.835	26087.5
		Ni	ppm	23.05	51	12	8.05	20
		Pb	ppm	14.65	56	1	11.93	13
		V	ppm	73.05	127	56	20.29	66.5

Catchment	Sample	Parameters	Units	Average	Maximum	Minimum	Standard deviation	Median
		Zn	ppm	60.6	91	27	14.40	60

In the Cheshmeh Kileh catchment, the amount of alkaline earth cations (Ca^{2+} and Mg^{2+}) is more dominant than alkaline cations (Na^{+} and K^{+}) in all samples. Strong acids (SO_4^{2-} + Cl^{-}) are superior to weak acids (CO_3^{2-} + HCO_3^{-}) in 5 samples from Seh-Hezar sub-river (CH1, CH2, CH4, CH5 and CH7) and in other samples weak acids are superior predominate strong acids. Study of the evolution process in the Cheshmeh Kileh Catchment showed Seh-Hezar sub-river starts from the joint of Maran and Darjan sub-rivers (samples CH1 and CH2) and then another sub-river (sample CH3) flows into it. In all three samples, calcium and magnesium cations (alkaline earth) are dominant, but strong acids are dominant in CH1 and CH2 samples and weak acids are dominant in CH3 sample. Next, the hydrochemical quality of CH4 to CH8 samples shows a combination of three upstream samples. CH1 sample is sulfate-calcic ($Ca\text{-}SO_4$) type and other samples in Seh-Hezar sub-river have bicarbonate-calcic ($Ca\text{-}HCO_3$) type. The high sulfate in CH1 is due to the dissolution of gypsum in the structure of the Karaj Formation located in Maran upstream. In Do-Hezar sub-river in all the samples (CH12, CH13, CH14, and CH15), alkaline earth cations prevail over alkalis and weak acids over strong acids, and carbonate hardness (secondary alkalinity) is more than 50%, as well as the samples have bicarbonate-calcic type. After sampling stations CH8 (Seh-Hezar) and CH15 (Do-Hezar), two sub-streams of Do-Hezar and Seh-Hezar join together, and samples CH16-CH23 were sampled on Cheshmeh Kileh river. Given that the CH16 sample was taken from the landfill leachate of Tonekabon, it has the least influence on the geologic structures of the region and in terms of hydrogeochemical composition, it is different from all the samples of the Cheshmeh Kileh Catchment and has a bicarbonate-sedic (Na-HCO3) type. The following samples represent a combination of two sub-rivers and in general of bicarbonate-calcic type (Fig. 7).

But in the Shiroud Catchment, in all samples, the amount of alkaline earth cations (Mg^{2+} and Ca^{2+}) is more dominant than alkaline cations (Na^{+} and K^{+}). In samples SH3-SH13, weak acids (HCO_3^{-} and CO_3^{2-}) are superior to strong acids (SO_4^{2-} and Cl^{-}) and carbonate hardness (secondary alkalinity) is more than 50%. But in the SH14 station sample, strong acids are more dominant than weak acids, and non-carbonate hardness (secondary salinity) is more than 50%. Study of the evolution process in the Shiroud Catchment showed that sample SH3, which is the most upstream station in this catchment, is of a bicarbonate-calcic ($Ca\text{-}HCO_3$) type, but sample SH4 (which is added to the main river from a branch) is carbonate-magnesic ($Mg\text{-}HCO_3$). At the next station, SH5, the water sample is of bicarbonate-calcic ($Ca\text{-}HCO_3$) type, indicating that the addition of the upstream subsidiary (station SH4) could not change the composition of the river, and the water type is still bicarbonate-calcic. In the estuary, sample SH14 is of chloric-calcic (Ca-Cl) type, which is caused by the advance of salty sea water in the Shiroud river (Fig. 7).

Figure 8 shows the chemistry of the cations and anions using Ternary diagrams. As shown, in the Cheshmeh Kileh Catchment, among the anions present in the samples, in the Seh-Hezar sub-river, at station CH1, sulfate is the predominant anion and the water is sulfated. CH2, CH4, and CH5 samples are non-dominant types of water. While the samples of CH3, CH6, CH7, and CH8 and the samples of the Do-Hezar sub-river and the Cheshmeh Kileh River are of the type of bicarbonate, and the bicarbonate ion is the dominant anion. Figure shows that in all samples except CH16, calcium ion is the dominant cation and the type of water is rich in calcium. In CH16 sample, sodium ion is dominant and of alkali-rich type. However, in the Shiroud Catchment, calcium cation is dominant in all samples and rich in calcium type. Also, in samples SH3-SH13, the dominant anion is bicarbonate, and only at station SH14, the dominant anion is chloride.

The Gibbs diagram gives a general idea about the intensity of water-rock chemical interaction. Gibbs [38] developed a model to investigate the mechanisms controlling the chemistry of surface waters and to understand their evolution, based on TDS parameters, $Na^{+}/(Na^{+}+Ca^{2+})$ and $Cl^{-}/(Cl^{-}+HCO_3^{-})$ using sum collected and analyzed samples from different parts of the world. Gibbs diagrams are used in many cases to determine the effect of effective processes such as precipitation, evaporation and weathering of bedrock on the chemical composition of surface water [39, 38].

According to the Gibbs diagram (Fig. 9), the factor controlling the water chemistry in the Cheshmeh Kileh Catchment is the chemical weathering of the minerals that make up the rocks. In both diagrams, sample CH16 is not in the range, indicating that this sample originates from the landfill leachate and is not of natural origin.

Based on the distribution and accumulation of points on the Gibbs diagram of the Shiroud Catchment (Fig. 9), in samples SH3-SH13, the factor controlling water chemistry is the dominance of weathering of the rocks and minerals. But sample SH14 shows the dominance of evaporation on water chemistry, which can confirm the infiltration of salty water from the Caspian Sea in the estuary of the Shiroud River.

The Stiff diagram is another graphical way to represent the chemistry of water. Hounslow (1995) published six patterns based on possible source rock and changes in the main elements of water, to compare the similarity or difference, which is a useful and quick solution to identify the possible source rock [40, 41]. According to Stiff diagram of the samples of the Cheshmeh Kileh Catchment (Fig. 10), in the Seh-

Hezar sub-river, CH1 samples originate from gypsum dominant lithology and CH2-CH8 samples originate from limestone dominant lithology. Also, as mentioned in the results of the Piper diagram, weak acids (bicarbonate) are more dominant than strong acids in CH3 sample. Limestone is the dominant lithology in the Do-Hezar sub-river. In the Cheshmeh Kileh, sample CH16 represents the severe changes resulting from the landfill leachate. But, after combining with the high volume of Cheshmeh Kileh river, the later samples have the dominant origin of limestone.

Based on Stiff diagram for the Shiroud catchment (Fig. 10) and Hounslow patterns, samples SH3 and SH5-SH13 originate from limestone lithology. This type of lithology is widespread throughout the catchment in unit $J_{2-3}^{l,dl}$ (Upper and Middle Jurassic), Nesen Formation Pn (Upper Permian), Ruteh Formation $P_r^{l,ml}$ (Upper Permian), unit P_d^l (Lower Permian), Dorud Formation $P_d^{s,sh}$ (Lower Permian) and Mobarak Formation $C_m^{l,ml}$ (Lower Carboniferous). Based on the Hounslow patterns, the SH4 station originates from basalt lithology. This lithology is observed in the sub-upstream of SH4 in the form of unit S^v of Silurian age. The shape of the Stiff diagram of the SH14 station shows the combination of salty sea water and atmospheric water (the chemical composition of the surface water of the river).

The amount of sulfate and chloride anions, and sodium and calcium cations; and the values of TDS and EC at the SH14 station show the phenomenon of the advancement of salt water and the mixing of sea water with fresh river water. It should be noted that the SH14 station was sampled inside the river due to the strength of the sea waves at the estuary. Based on the Piper diagram (Fig. 7), the water at this station is of chloric-calcic type. Ternary diagram (Fig. 8) also shows that water in SH14 is of chloric type. Also, the SH14 sample shows Evaporation Dominance on the chemical composition in the Gibbs diagram (Fig. 9). While in other samples, Rock Weathering Dominance prevails. According to several studies that have been conducted in the past years, factors such as the increase in sea water level [15], changes in river flow rate [42], undesired dredging of sand and gravel, and changes in tides and in wind direction [43] can be considered as the causes of this phenomenon. According to previous studies on the Shiroud River [44], the factors affecting this river are repeated and wrong dredging, excessive sand and gravel harvesting from the riverbed, and many sand mines (in the flood plains and near the estuary).

4.2 Quality evaluation of irrigation and industry

4.2.1 Industrial use potential

According to the calculated results (Table 5) for the Cheshmeh Kileh Catchment, the Langelier Saturation Index (LSI) was positive at stations CH1 and CH16, which is characteristic of supersaturated water and tends to deposit $CaCO_3$. In other samples, LSI < 0 and the water is under saturation and the water has the potential to decompose $CaCO_3$. Therefore, according to the LSI, apart from CH1 and CH16 stations, other stations are suitable for industrial use. Based on the Ryznar Saturation Index (RSI), all stations have saturated water and have the potential to decompose $CaCO_3$. According to the Puckorius Scaling Index (PSI), all stations tend to deposit sediments and are not suitable for industrial use due to sedimentation in industrial facilities. Corrosion Rate (CR) at stations CH1, CH2, CH4, CH5 and CH7 was CR > 1 and water transportation with metal pipes is not allowed. When using other stations for industrial use, water transfer with any type of pipe is unobstructed. Based on the Larson-Skold Index (L-SI), stations CH1, CH2 and CH4 have high corrosive. Also, at stations CH5, CH6 and CH7 $0.8 < L\text{-}SI < 1.2$ and highly corrosive. Other stations had no corrosive.

But in the Shiroud Catchment (Table 6), according to the Langelier Saturation Index (LSI), all stations have supersaturated water and tend to deposit $CaCO_3$. Based on Ryznar Saturation Index, stations SH4 and SH6 are neutral, and other stations have saturated water and have the potential to decompose $CaCO_3$. According to the Puckorius Scaling Index, all stations tend to be corrosive. Based on the CR, water transfer is unhindered at all stations except SH14 station with any type of pipe. It is not allowed to transfer water with metal pipe at SH14 station. According to the LSI, SH14 station has high corrosive and other stations have no corrosive. Given that due to the advance of salty water in the estuary of the Shiroud River, the chemical composition of the water at the SH14 station follows the chemical characteristics of the Caspian Sea water, the corrosion rate at this station is high and for the construction of metal and reinforced concrete structures - in which metals are used to strengthen the concrete's strength - was prevented from causing subsequent damages with caution and further detailed studies.

Table 5
Calculated results of irrigation and industrial indices in the Cheshmeh Kileh catchment.

sample	Irrigation indexes									Industrial indexes				
	PS	RSBC	TH	KR	PI	MH	RSC	SAR	SSP	L-SI	CR	PSI	RSI	LSI
CH1	5/76	-7/34	32/3	0/09	21/73	12/9	-7/88	0/44	8/73	2/47	2/71	1/07	8/67	0.05
CH2	2/18	-1/12	10/69	0/09	41/7	20/07	-1/38	0/25	9/12	1/2	1/47	3/25	10/01	-0/6
CH3	1/79	0/47	14/88	0/03	40/56	37/79	-0/71	0/09	4/22	0/57	0/71	2/03	10/18	-1
CH4	2/505	-1/6	13/25	0/10	37/31	21/46	-1/90	0/32	10/27	1/28	1/53	2/7	9/7	-0/41
CH5	2/475	-1/72	13/64	0/10	36/43	21	-1/73	0/31	10/05	1/12	1/35	2/56	9/70	-0/45
CH6	2/135	-1/06	13/48	0/12	41/29	23/45	-1/03	0/38	11/94	0/82	1	2/19	9/90	-0/71
CH7	2/12	-1/17	13/28	0/12	40/46	23/38	-1/42	0/36	11/54	0/93	1/11	2/34	10/16	-0/93
CH8	2/12	-1/07	13/81	0/12	40/53	23/54	-0/77	0/36	11/27	0/74	0/88	2/25	10/49	-1/28
CH12	1/4	-0/02	13/12	0/04	41/91	32/18	-0/62	0/13	4/76	0/46	0/59	1/89	10/49	-1/30
CH13	1/40	0/83	12/24	0/04	48/51	33/5	0/28	0/11	4/24	0/36	0/48	1/90	10/41	-1/2
CH14	1/38	1/46	13/33	0/05	50/35	33/48	0/89	0/15	5/69	0/32	0/41	1/77	10/50	-1/33
CH15	1/36	1/07	13/57	0/06	48/11	32/52	2/2	0/17	6/07	0/25	0/31	1/74	10/26	-1/11
CH16	6/00	64/97	20/96	2/18	110/02	53/12	61/65	7/69	77/78	0/09	0/12	-3/05	8/14	0/19
CH17	1/85	0/18	14/7	0/13	46/31	25/99	-0/8	0/41	13/90	0/57	0/71	1/81	9/76	-0/65
CH18	1/66	0/28	13/79	0/10	46/56	25/53	-0/5	0/31	10/14	0/53	0/65	1/86	9/7	-0/56
CH19	1/6	2/16	12/07	0/06	57/84	30/44	0/93	0/18	6/83	0/34	0/47	1/61	9/94	-0/79
CH20	1/34	1/06	13/06	0/05	48/82	34/34	0/05	0/16	5/97	0/37	0/48	1/86	9/77	-0/57
CH21	1/83	0/19	13/44	0/09	46/19	26/30	-0/69	0/28	9/40	0/61	0/75	1/89	9/76	-0/61
CH22	2	0/37	15/85	0/08	43/37	24/22	-0/96	0/27	8/38	0/60	0/73	1/72	9/73	-0/65
CH23	1/81	0/3	15/01	0/09	44/2	27/65	-1/11	0/29	9/22	0/59	0/73	1/62	9/85	-0/76
Mean	2.24	2.91	14.83	0.19	46.61	28.14	2.22	0.63	12	0.71	0.86	1.75	9.86	-0.73
Min	1.34	-7.34	10.69	0.03	21.73	12.9	-7.88	0.09	4.22	0.09	0.12	-3.05	8.67	-1.33
Max	6.00	64.97	20.96	2.18	110.02	53.12	61.65	7.69	77.78	2.47	2.71	3.25	10.50	0.19
Ave	2.24	2.91	14.83	0.19	46.61	28.14	2.22	0.63	12	0.71	0.86	1.75	9.86	-0.73
SD	1.3	14.74	4.57	0.47	16.52	8.41	14.12	1.66	15.73	0.52	0.57	1.22	0.58	0.41

Table 6
Calculated results of irrigation and industrial indices in the Shiroud catchment.

sample	Irrigation indexes									Industrial indexes				
	PS	RSBC	TH	KR	PI	MH	RSC	SAR	SSP	L-SI	CR	PSI	RSI	LSI
SH3	1/48	-0/08	194/81	0/05	42/94	34/67	-0/91	0/14	5/64	-101/1	0/51	7/65	7/13	0/81
SH4	1/32	2/08	224/91	0/05	48/73	50/53	0/06	0/16	6/09	-210/29	0/29	7/44	6/95	0/97
SH5	1/71	1/05	208/13	0/05	47/57	40/45	0/02	0/15	5/79	-161/62	0/41	7/58	7/03	0/90
SH6	1/07	1/25	205/94	0/05	49/17	40/45	0/14	0/15	5/88	-192/14	0/27	7/53	7	0/92
SH7	1/40	1/11	210/38	0/09	52/84	25/71	0/62	0/25	8/51	-218/88	0/28	7/25	7/11	0/69
SH8	1/66	1/22	200/34	0/1	53/97	31/88	-0/06	0/28	10/00	-159/12	0/42	7/65	7/48	0/45
SH9	1/3	0/06	208/76	0/1	46/09	31/89	-0/91	0/29	10/25	-115/37	0/46	7/71	7/30	0/64
SH10	1/50	1/02	230/24	0/09	49/15	30/23	-0/38	0/28	9/65	-179/68	0/37	7/38	7/63	0/2
SH11	1/50	0/47	230/55	0/09	45/64	32/70	-0/61	0/27	9/1	-152/43	0/42	7/45	7/15	0/70
SH12	1/42	2/24	205/43	0/09	58/19	32/83	0/89	0/27	9/7	-234/05	0/29	7/23	7/69	0/13
SH13	1/24	1/90	226/57	0/09	53/09	32/78	0/41	0/27	9/16	-234/81	0/27	7/28	7/22	0/59
SH14	84/44	1/82	260/45	0/18	52/31	35/87	-0/06	0/60	16/53	3176/75	14/65	7/34	7/57	0/3
Min	1/07	-0/08	194/81	0/05	42/94	25/71	-0/91	0/14	5/64	-234/81	0/27	7/23	6/95	0/13
Max	84/44	2/24	260/45	0/18	58/19	50/53	0/89	0/60	16/53	3176/75	14/65	7/71	7/69	0/97
Ave	8.33	1.18	217.21	0.08	49.97	34.99	-0.06	0.26	8.86	101.44	1.55	7.46	7.27	0.61
SD	23.97	0.75	18.13	0.04	4.25	6.36	0.56	0.12	3.01	969.43	4.12	0.17	0.26	0.28

4.2.2 Irrigation use potential

Tables 5 and 6 shows the results of the calculations for the quality indices of irrigation. The Soluble Sodium Percentage (SSP) at the CH16 station (77.78) is in the permissible-poor range. At other stations, the value of SSP is in the Excellent range. The calculated value of Sodium Adsorption Ratio (SAR) indicates that the value of this index is excellent at all stations. Based on the Residual Sodium Carbonate (RSC), the station CH15 has fair quality and station CH16 is poor-unsuitable. Also, the Residual Sodium Bi-Carbonate (RSBC) index has been evaluated to be Unsatisfactory at the CH16 station. According to the Magnesium Hazard (MH) at the CH16 station, the water quality is unsuitable and harmful for the soil. Also, Based on the Permeability Index (PI), water quality at the CH14, CH16 and CH19 stations are unsuitable for Irrigation use. The Kelly's Ratio (KR) at the CH16 station was excess and unsuitable. The Potential Salinity (PS) at stations CH1 is unsuitable due to high sulfate and CH16 due to high chlorine. Based on the Total Hardness (TH), all the stations have soft water and are suitable for agricultural use. Also, the TDS at the CH16 station are not considered for freshwater and are not suitable for agricultural use. According to Electrical Conductivity (EC) reported by the laboratory, the amount of EC at the CH1 station is in the permissible range and in the doubtful range at station CH16. Other stations were classified as good.

According to the calculations in the Shiroud catchment (Table 6), SSP and SAR are in the excellent range. In terms of MH, all the stations are Suitable for irrigation except SH4 (MH = 50.53). Given that all the stations are in $25 < PI < 75$, they do not have suitable conditions for irrigation. All stations are suitable according to KR classification. According to the TH, all stations are considered hard waters. In terms of RSBC, all stations are considered in the safe range. Based on the PS, all stations except SH14 are in the suitable range and SH14 is in the unsuitable range. All stations have TDS as freshwater, but the SH14 station is not in this range. Also, in terms of EC, all stations except SH14 are in the good range. SH14 has unsuitable EC.

Electrical conductivity is one of the important parameters in agricultural sciences and plant nutrition related sciences. According to the agricultural industry in northern Iran (the southern shores of the Caspian Sea), kiwi, citrus fruits and rice are the dominant crops in the study area. Several studies have been conducted on the optimal EC for rice cultivation. Among the studies conducted in the world, Castillo et al. 2007 [45], Asch et al. 2000 [46], Zeng and Shannon 2000 [47] and Sultana et al. 1999 [48] can be mentioned. In these studies, salinities between 1.1 and 2 deci-siemens per meter have been reported as levels of irrigation water salinity that do not reduce rice yield. But in greenhouse and hydroponic cultivation, the plant is more dependent on the chemical composition of water. Savvas and Gruda 2018 believed that soilless cultivation systems (SCS) or hydroponic cultivation is a new technology in the modern greenhouse industry. The main advantage of SCS is the independence of the product from the soil, which, as a heterogeneous natural environment, is highly sensitive to saline and sodic. The most widely used hydroponic products include vegetables, fruits and cut flowers. In this type of cultivation, the plant is fed through nutrient solution (NS) at the same time as irrigation. Fertilizer unit is very important for SCS because it acts as an automatic system for precise dosing of fertilizers to irrigation water. The NS process is controlled by monitoring the EC and pH of the output solution. Therefore, the exact NS is determined according to the initially measured EC and pH values [49].

The United States Salinity Laboratory (USSL) diagram is used to evaluate the suitability of water. The USSL diagram is constructed by plotting the Sodium Absorption Ratio (SAR) values against the Electrical Conductivity (EC) data in a semi-logarithmic two-dimensional diagram (Fig. 11). The classification of four classes of each salinity and SAR is presented in Table 7 [50, 27].

Table 7
Electrical conductivity (EC) and sodium absorption ratio (SAR) values and salinity classification for agricultural use [27].

salinity hazard	Classification	EC (μS/cm)	salinity hazard	Classification	SAR
Low	C1	< 250	Low	S1	< 10
Medium	C2	250–750	Medium	S2	10–18
High	C3	750–2250	High	S3	18–26
Very High	C4	> 2250	Very High	S4	> 26

According to Fig. 11, In the Cheshmeh Kileh catchment, CH1 sample is in C_3S_1 category and CH16 sample is in C_4S_1 category. This means that the CH1 sample has a high risk in terms of electrical conductivity and a low risk in terms of SAR salinity risk for agricultural uses. CH16 sample shows a high risk of salinity in terms of electrical conductivity, but it has a low risk in terms of SAR. Other samples are in the C_2S_1 category, which indicate moderate salinity risk in terms of electrical conductivity and low risk in terms of SAR.

But in the Shiroud catchment, samples SH3-SH13 have C_2S_1 category and moderate salinity risk in terms of electrical conductivity and low risk in terms of SAR. SH14 sample is in the C_4S_1 category, which means that SH14 sample has a very high risk in terms of electrical conductivity and a low risk in terms of SAR.

Based on Wilcox's classification (1955), the Wilcox diagram is divided into 4 categories: excellent to good, good to permissible, permissible to unsuitable, and unsuitable by plotting the percentage of soluble sodium (SSP) versus electrical conductivity (EC) [22].

According to the Wilcox diagram of the samples in the Cheshmeh Kileh catchment (Fig. 12), sample CH16 is in the unsuitable category, sample CH1 is in the good to permissible category, and the other samples are in the excellent to good category. But in the Shiroud catchment, samples SH3-SH13 have the excellent to good category and sample SH14 is in the unsuitable category.

4.3 Heavy metals evaluation index in water

Table 8 shows the results of the indices of heavy metals in the water of the Cheshmeh Kileh and Shiroud Catchments.All of samples have low pollution. In the Cheshmeh Kileh Catchment, the highest values of Heavy metals Evaluation Index (HEI) were calculated at CH20 < CH1 < CH14 < CH17 < CH18 < CH2 < CH16. Stations CH16, CH17 and CH18 are landfill leachate and post-landfill, respectively. At the CH16 station, the highest amount of Aluminum, Arsenic, Chromium, Iron, Manganese, Nickel, Lead, Vanadium and Zinc was recorded compared to other stations.

But in the Shiroud Catchment, the highest values of HEI were calculated at SH13 < SH9 < SH14 < SH7. At these stations, due to the recording of Se, they have a higher HEI value than other stations. These stations are affected by the industrial activity of sand mines and leaching operations in these mines. The resulting leachate is poured into the river.

The Degree of Contamination index (C_d) in all samples has low pollution. In the Cheshmeh Kileh Catchment, the highest values of C_d were calculated at CH22 < CH121 < CH17 < CH13 < CH16; and in the Shiroud catchment were calculated at SH10 < SH6 < SH3 < SH12 < SH5 < SH4.

Table 8
Calculated results of heavy metal indices (water) in the Cheshmeh Kileh and Shiroud catchment.

sample	HEI	C_d	Results
SH3	0.45	-4.54	HEI:
SH4	0.69	-4.30	SH6 < SH3 < SH12 < SH8 = SH5 < SH11 < SH10 < SH4 < SH13 < SH9 < SH14 < SH7
SH5	0.55	-4.44	C_d:
SH6	0.44	-4.56	SH13 < SH9 < SH8 < SH11 < SH14 < SH7 < SH10 < SH6 < SH3 < SH12 < SH5 < SH4
SH7	0.91	-5.09	
SH8	0.55	-5.45	
SH9	0.89	-6.11	
SH10	0.62	-4.75	
SH11	0.56	-5.44	
SH12	0.52	-4.48	
SH13	0.79	-6.21	
SH14	0.9	-5.38	
CH1	0.8	-8.20	HEI:
CH2	1.30	-5.72	CH13 < CH12 = CH15 < CH6 < CH4 < CH23 = CH7 < CH8 < CH22 < CH5 < CH21
CH3	0.76	7.23	<CH19 < CH3 < CH20 < CH1 < CH14 < CH17 < CH18 < CH2 < CH16
CH4	0.54	-7.45	C_d:
CH5	0.66	-7.34	CH1 < CH4 < CH5 < CH3 < CH12 < CH8 < CH6 < CH19 < CH20 < CH18 < CH14
CH6	0.51	-6.35	<CH2 < CH15 < CH7 = CH23 < CH22 < CH121 < CH17 < CH13 < CH16
CH7	0.58	-5.42	
CH8	0.6	-6.40	
CH12	0.47	-6.52	
CH13	0.42	-4.57	
CH14	0.86	-5.81	
CH15	0.47	-5.53	
CH16	10.04	0.045	
CH17	0.92	-5.08	
CH18	1.1	-5.90	
CH19	0.72	-6.27	
CH20	0.79	-6.21	
CH21	0.69	-5.31	
CH22	0.63	-5.36	
CH23	0.58	-5.42	

4.4 Heavy metals evaluation index in sediment

Table 9 shows the results of calculations of heavy metal indices in the sediments of Cheshmeh Kileh and Shiroud catchments. According to the Geological Accumulation Index (I_{geo}), in the Cheshmeh Kileh Catchment, the highest average pollution is Ni < Cu < Cr < V < Zn = Pb < Cd. While in the Shiroud Catchment, Ni < Cu < Pb < Cr < Cd < V < Zn have the highest average pollution.

Based on Enrichment factor (EF), in Cheshmeh Kileh catchment area, the highest average enrichment was for Ni < Cr < Cu < V < Zn < Pb < Cd. But in the Shiroud Catchment, the highest average enrichment was for Ni < Cu < Pb < Cd < Cr < V < Zn.

According to CF, in the Cheshmeh Kileh Catchment, the highest average pollution was for Cr < Ni < V < Cu < Zn < Pb < Cd, and in the Shiroud Catchment for Cr < Ni < V < Cu < Zn < Pb < Cd.

It should be noted that in the Cheshmeh Kileh Catchment, the CH16 station (landfill leachate) has the highest heavy metal pollution.

Table 9
Calculated results of heavy metal indices (sediment) in the Cheshmeh Kileh and Shiroud catchment.

Index	HM	Catchment	descriptive statistics		Results
CF	Cd	Shiroud	Min	0	Cheshmeh Kileh:
			Max	3	Cr < Ni < V < Cu < Zn < Pb < Cd
			Average	1.58	Shiroud:
		Cheshmeh Kileh	Min	1	Cr < Ni < V < Cu < Zn < Pb < Cd
			Max	6	
			Average	2.8	
	Cr	Shiroud	Min	0.63	
			Max	1.17	
			Average	0.88	
		Cheshmeh Kileh	Min	0.34	
			Max	1.32	
			Average	0.521	
	Cu	Shiroud	Min	0.63	
			Max	2.1	
			Average	1.075	
		Cheshmeh Kileh	Min	0.53	
			Max	2.3	
			Average	0.92	
	Ni	Shiroud	Min	0.6	
			Max	1.2	
			Average	0.96	
		Cheshmeh Kileh	Min	0.3	
			Max	1.275	
			Average	0.58	
	Pb	Shiroud	Min	0.2	
			Max	2.2	
			Average	0.925	
		Cheshmeh Kileh	Min	0.1	
			Max	56	
			Average	1.465	
	V	Shiroud	Min	1.1	
			Max	1.825	
			Average	1.40	
		Cheshmeh Kileh	Min	0.7	
			Max	1.59	
			Average	0.91	

Index	HM	Catchment	descriptive statistics		Results
	Zn	Shiroud	Min	1.1	
			Max	2.16	
			Average	1.67	
		Cheshmeh Kileh	Min	0.54	
			Max	1.82	
			Average	1.212	
EF	Cd	Shiroud	Min	0	Cheshmeh Kileh:
			Max	1.61	Ni < Cr < Cu < V < Zn < Pb < Cd
			Average	0.84	Shiroud:
		Cheshmeh Kileh	Min	0.90	Ni < Cu < Pb < Cd < Cr < V < Zn
			Max	6.11	
			Average	2.55	
	Cr	Shiroud	Min	0.56	
			Max	1.44	
			Average	0.99	
		Cheshmeh Kileh	Min	0.70	
			Max	1.32	
			Average	0.92	
	Cu	Shiroud	Min	0.37	
			Max	1.19	
			Average	0.64	
		Cheshmeh Kileh	Min	0.56	
			Max	0.83	
			Average	0.93	
	Ni	Shiroud	Min	0.32	
			Max	0.67	
			Average	0.57	
		Cheshmeh Kileh	Min	0.29	
			Max	0.84	
			Average	0.56	
	Pb	Shiroud	Min	0.17	
			Max	1.9	
			Average	0.83	
		Cheshmeh Kileh	Min	0.16	
			Max	8.53	
			Average	2.09	
	V	Shiroud	Min	1.0	
			Max	1.56	

Index	HM	Catchment	descriptive statistics		Results
			Average	1.25	
		Cheshmeh Kileh	Min	1.12	
			Max	1.82	
			Average	1.31	
	Zn	Shiroud	Min	0.96	
			Max	1.66	
			Average	1.33	
		Cheshmeh Kileh	Min	0.93	
			Max	2.00	
			Average	1.58	
I_{geo}	Cd	Shiroud	Min	-1.58	Cheshmeh Kileh:
			Max	0	Ni < Cu < Cr < V < Zn = Pb < Cd
			Average	-0.67	Shiroud:
		Cheshmeh Kileh	Min	0	Ni < Cu < Pb < Cr < Cd < V < Zn
			Max	1	
			Average	0.38	
	Cr	Shiroud	Min	-1.25	
			Max	-0.36	
			Average	-0.79	
		Cheshmeh Kileh	Min	-2.14	
			Max	-0.18	
			Average	-1.61	
	Cu	Shiroud	Min	-2.12	
			Max	-0.39	
			Average	-1.47	
		Cheshmeh Kileh	Min	-2.37	
			Max	-0.26	
			Average	-1.70	
	Ni	Shiroud	Min	-2.23	
			Max	-1.23	
			Average	-1.58	
		Cheshmeh Kileh	Min	-3.22	
			Max	-1.14	
			Average	-2.35	
	Pb	Shiroud	Min	-3.23	
			Max	0.23	
			Average	-1.40	
		Cheshmeh Kileh	Min	-4.23	

Index	HM	Catchment	descriptive statistics		Results
			Max	1.58	
			Average	-0.84	
	V	Shiroud	Min	-0.77	
			Max	-0.04	
			Average	-0.44	
		Cheshmeh Kileh	Min	-1.42	
			Max	-0.24	
			Average	-1.08	
	Zn	Shiroud	Min	-0.93	
			Max	0.04	
			Average	-0.35	
		Cheshmeh Kileh	Min	-1.96	
			Max	-0.21	
			Average	-0.84	

4.5 Cluster analysis of heavy metals

Ward's method used hierarchical clustering to classify samples based on heavy metal concentration. The results of this investigation are shown in the form of a dendrogram in Figs. 13 and 14. Based on the concentration of heavy metals in the surface water of the Cheshmeh Kileh catchment, the samples are classified into two general clusters. This dendrogram shows that the concentration of heavy metals in sample CH16 is different from other samples. Sediment samples are also classified into two main clusters. Sample CH16 and samples CH1 and CH2 were classified in a separate cluster compared to other samples. The difference between these samples can be related to the landfill station (CH16) and the predominance of igneous and metamorphic lithology above samples CH1 and CH2.

The samples in the surface water of Shiroud catchment are divided into two main clusters. One cluster includes SH4 sample (basalt to andesibasalt lithology) and the other cluster is divided into two sub-clusters. However, in sediment samples, the clustering of samples does not match with the clustering of water samples. This shows that the conditions for the dissolution of elements and the transfer of metals from sediment to water are not inevitable.

5. Conclusion

Based on the hydrogeochemical studies conducted on the water samples, the dominant type in both Catchments is calcium bicarbonate, but in the Cheshmeh Kileh Catchment, the CH1 station, under the influence of gypsum lithology in the Karaj Formation upstream of this station, has a sulfate-carbonated composition. Also, the CH16 station, which was the landfill leachate is of bicarbonate-sodic type. However, in the Shiroud Catchment, the SH4 station affected by basalt lithology is of magnesic-bicarbonate type. Also, the SH14 station (the estuary) is of chloric-calsic type due to the mixing of salt water and river water.

Given the distribution and accumulation of points on the Gibbs diagram, the factor of controlling water chemistry is the dominance of weathering and constituent minerals of rocks. However, in the Cheshmeh Kileh Catchment, the CH16 station is out of range in both diagrams, indicating that this station originates from the landfill leachate and does not have a natural origin. Also, in the Shiroud Catchment, the SH14 station shows the dominance of evaporation on water chemistry, which can confirm the infiltration of the Caspian sea salt water in the estuary of the Shiroud River.

Given the Stiff diagram of the samples in the Cheshmeh Kileh Catchment, in the Seh-Hezar sub-river, station CH1 originates from the dominant lithology of gypsum (Karaj Formation) and stations CH2-CH8 originate from the dominant lithology of limestone. Limestone is the dominant lithology in the Do-Hezar sub-river. In Cheshmeh Kileh river, station CH16 shows severe changes resulting from landfill leachate. But, after combining with the high volume of Cheshmeh Kileh river, next stations have the dominant source of limestone. In the Shiroud Catchment, stations SH3 and SH5 to SH13 originate from limestone lithology. Based on the Hounslow patterns, the SH4 station originates from basalt lithology. This lithology is observed in the sub-upstream of SH4 in the form of S^v unit of Silurian age. The shape of the Stiff diagram of the SH14 station shows the combination of sea salt water and atmospheric water (the chemical composition of the surface water of the river).

According to the researchers' studies, many reasons have been mentioned for the advance of the salt water of the sea in the freshwater of the river. Also, according to the studies conducted by Hosseinzadeh et al. (2018) on the Shiroud River, the effects of improper sand and gravel harvesting from this river have been confirmed. Repeated and wrong dredging, excessive sand and gravel harvesting from the riverbed, and many sand mines (in the plains and near the estuary) have caused the infiltration of salt water in the Shiroud River.

In the Cheshmeh Kileh Catchment, at stations CH1 and CH16, the water tends to precipitate $CaCO_3$ and are not suitable for industrial use. The Puckorius index shows that all the samples have a tendency to deposit and are not suitable for industrial use due to depositing in industrial facilities. Based on CR, stations CH1, CH2, CH4, CH5 and CH7 are not allowed to transfer water with metal pipes. Based on the LSI, stations CH1, CH2 and CH4 have high corrosive. Also, stations CH5, CH6 and CH7 have high corrosive. But in the Shiroud Catchment, based on the LSI, all stations tend to deposit calcium carbonate. Based on Ryznar saturation index, SH4 and SH6 stations are neutral and other stations with water are under saturation. According to the Pokorios index, all stations tend to be corrosive. It is not allowed to transfer water with metal pipe at the SH14 station. According to the LSI, station SH14 has high corrosive. Given that the chemical composition of SH14 station follows the chemical characteristics of Caspian sea water due to the advance of salty water in the mouth of Shiroud river, corrosion rate in this station is high and for the construction of metal and reinforced concrete structures further detailed studies are needed to prevent subsequent damages.

According to the quality indices of irrigation, in the Cheshmeh Kileh Catchment, the CH16 station has poor quality for most of the indices. The PS at stations CH1 is unsuitable due to high sulfate and CH16 due to high chlorine ion. The amount of EC at station CH1 is in the permissible range and at CH16 station is in the doubtful range. In the Shiroud Catchment, station SH4 is unsuitable for irrigation in terms of MH (due to high magnesium). Given that all the stations are in the range of $25 < PI < 75$, they do not have suitable conditions for irrigation. Based on TDS, station SH14 is not in freshwater range and EC is unsuitable.

The evaluation of heavy metals in water showed the highest average heavy metal evaluation index at stations CH16 (landfill), CH17, CH18 (after landfill), respectively. At station CH16, the highest amount of Aluminum, Arsenic, Chromium, Iron, Manganese, Nickel, Lead, Vanadium, and Zinc was recorded compared to other stations in the Cheshmeh Kileh Catchment. But in the Shiroud Catchment, the highest values of HEI were calculated SH13 < SH9 < SH14 < SH7 respectively. The stations, due to the recording of Se had a higher HEI value than other stations. These stations are affected by the industrial activity of sand mines and leaching operations in these mines. Also, the Degree of Contamination index (C_d) in all samples has low pollution.

According to the I_{geo}, in the Cheshmeh Kileh Catchment, the highest average heavy metal pollution in the sediments is Ni < Cu < Cr < V < Zn = Pb < Cd. While in the Shiroud Catchment, Ni < Cu < Pb < Cr < Cd < V < Zn have the highest average heavy metal pollution. Based on the enrichment factor, in the Cheshmeh Kileh Catchment, the highest average enrichment is Ni < Cr < Cu < V < Zn < Pb < Cd. But in the Shiroud Catchment, the highest average enrichment is Ni < Cu < Pb < Cd < Cr < V < Zn. In the Cheshmeh Kileh Catchment, station CH16 (landfill effluent) had the highest heavy metal pollution.

Declarations

Acknowledgements

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Figures

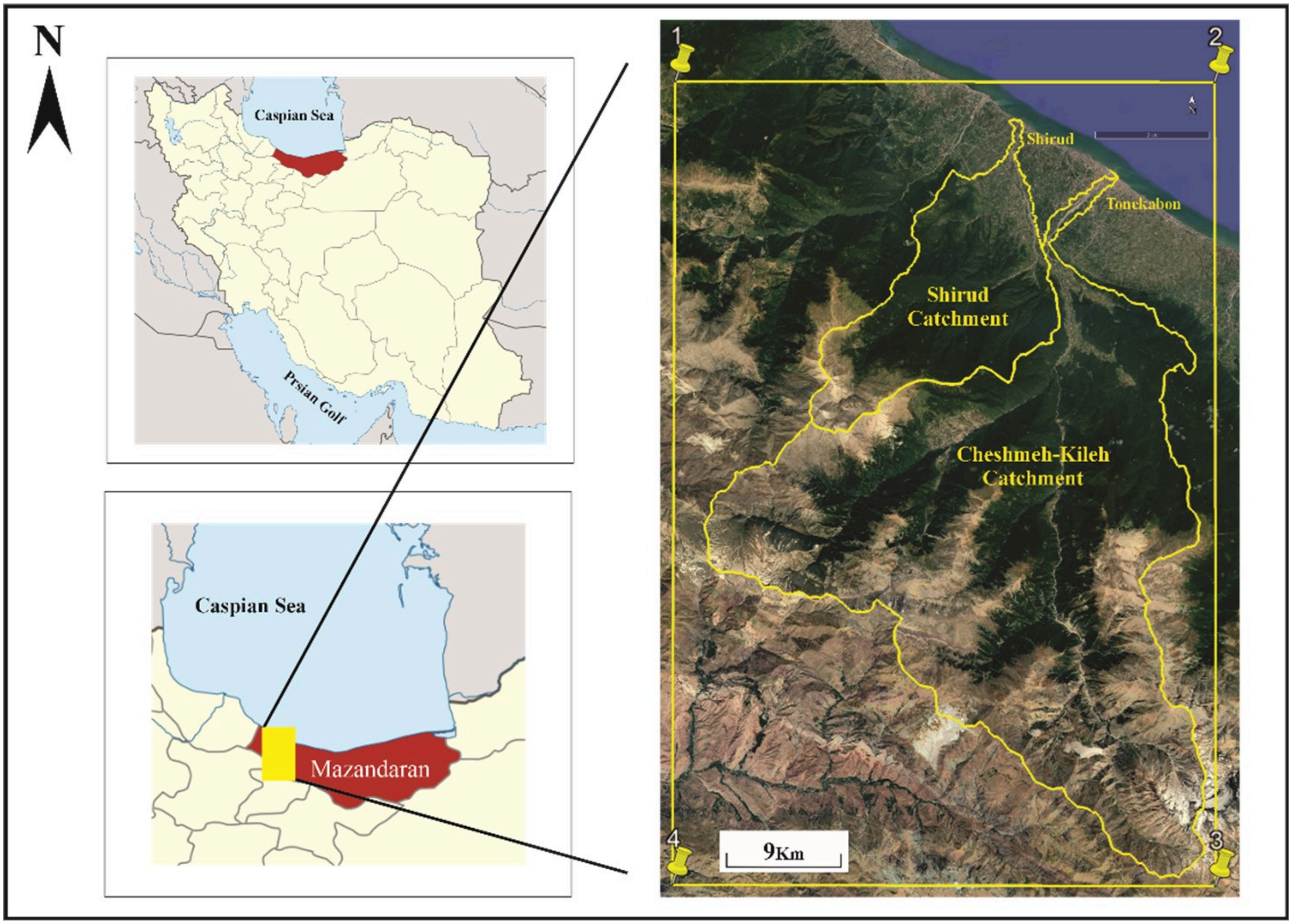

Figure 1

Locations of study area

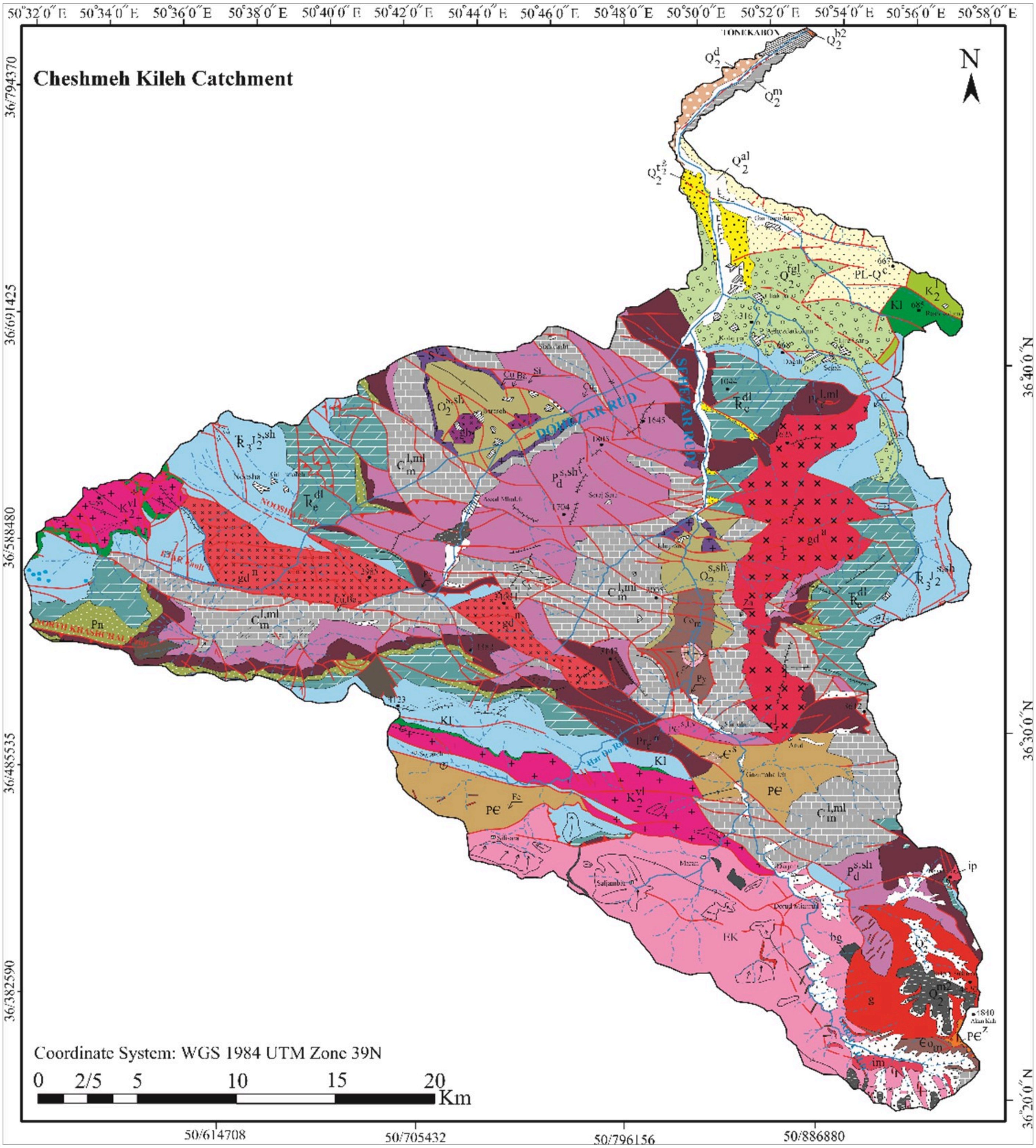

Figure 2

Geological map of Cheshmeh Kileh catchment (Redesigned from two sheets (6163 and 6162) of geological maps, published by the Geological Survay and Mineral Exploration Organization of Iran) [13, 14].

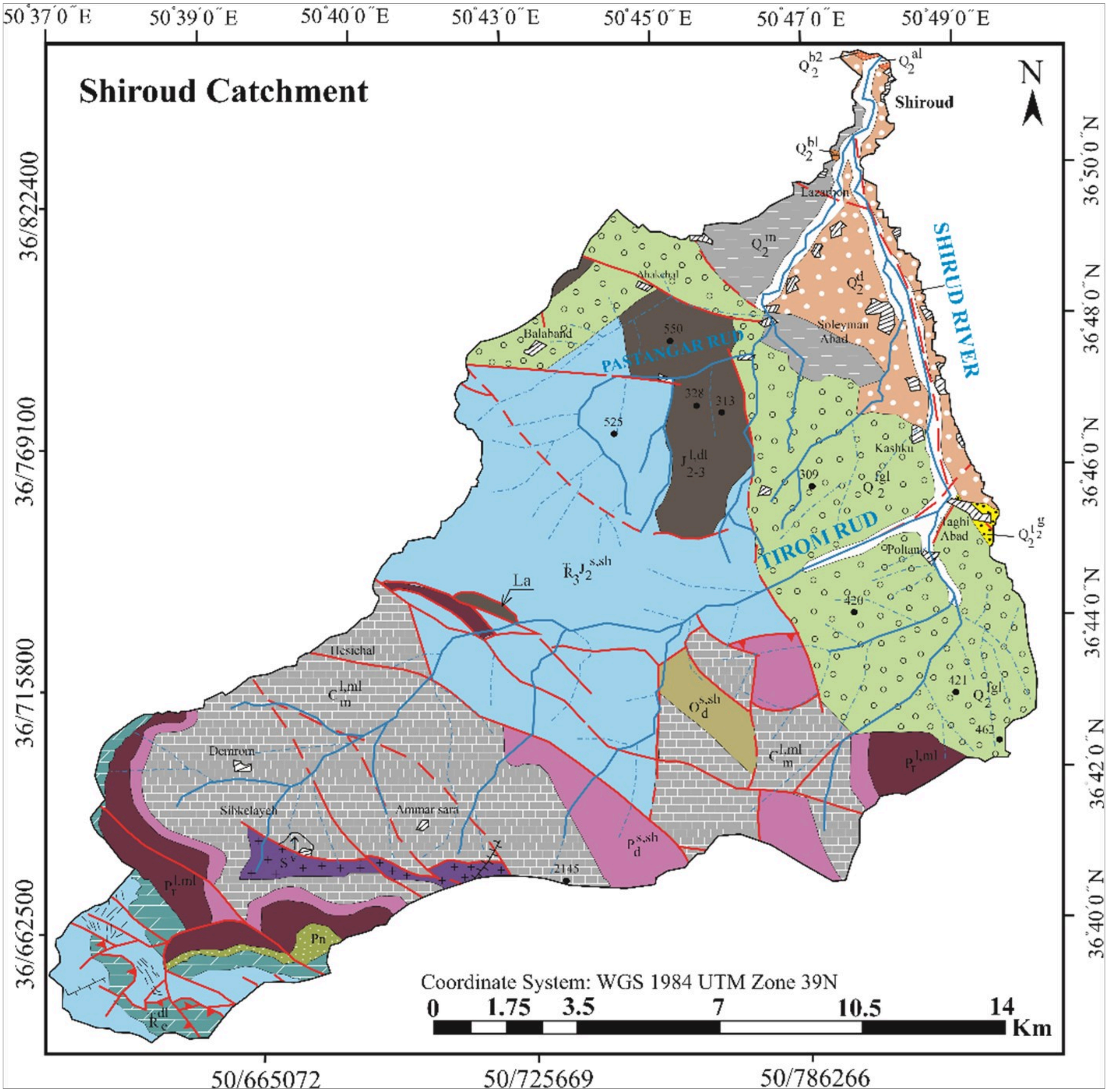

Figure 3

Geological map of Shiroud catchment (Redesigned from one sheet (6163) of geological maps, published by the Geological Survay and Mineral Exploration Organization of Iran) [13].

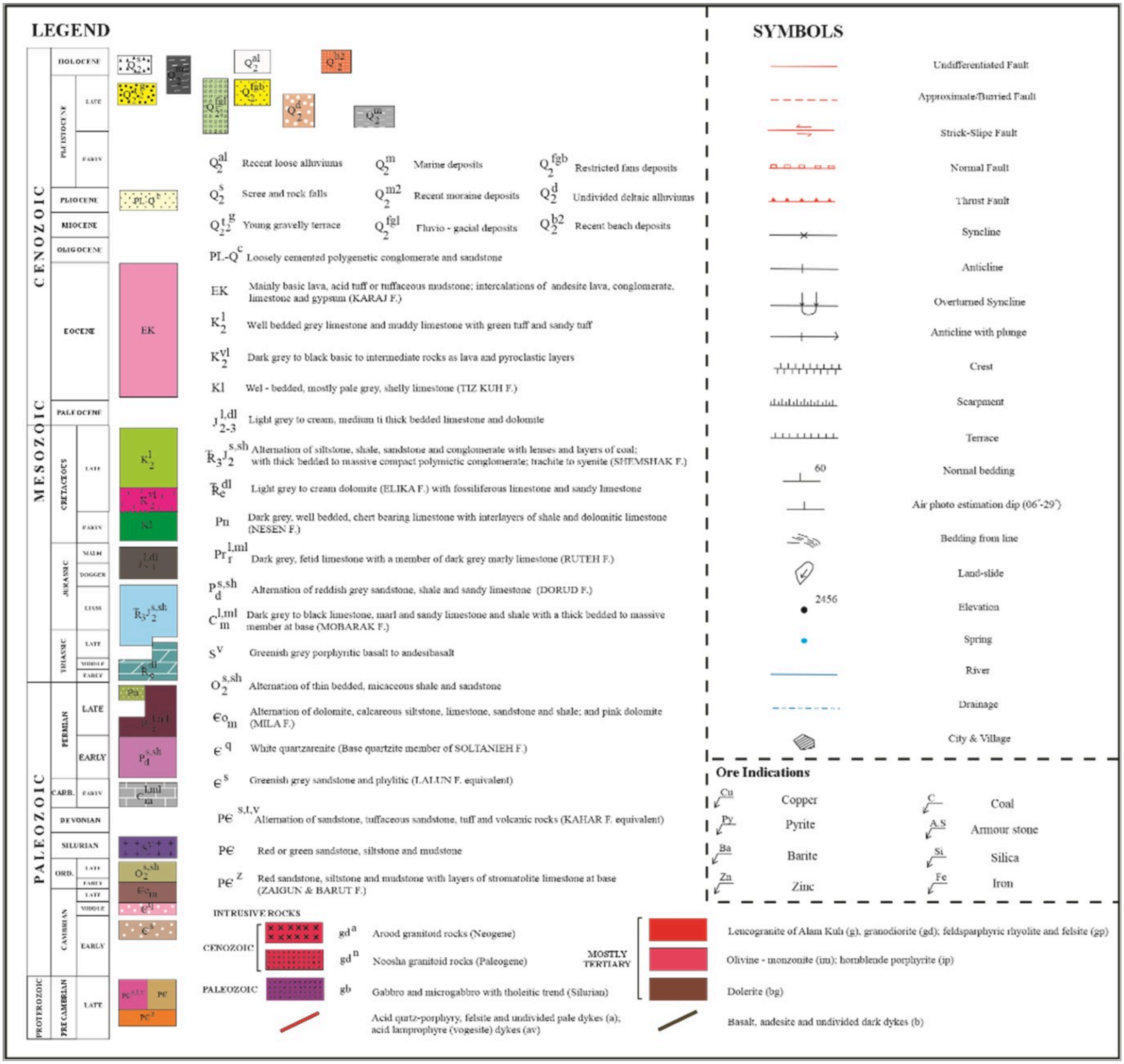

Figure 4

Legend of geological maps [13, 14].

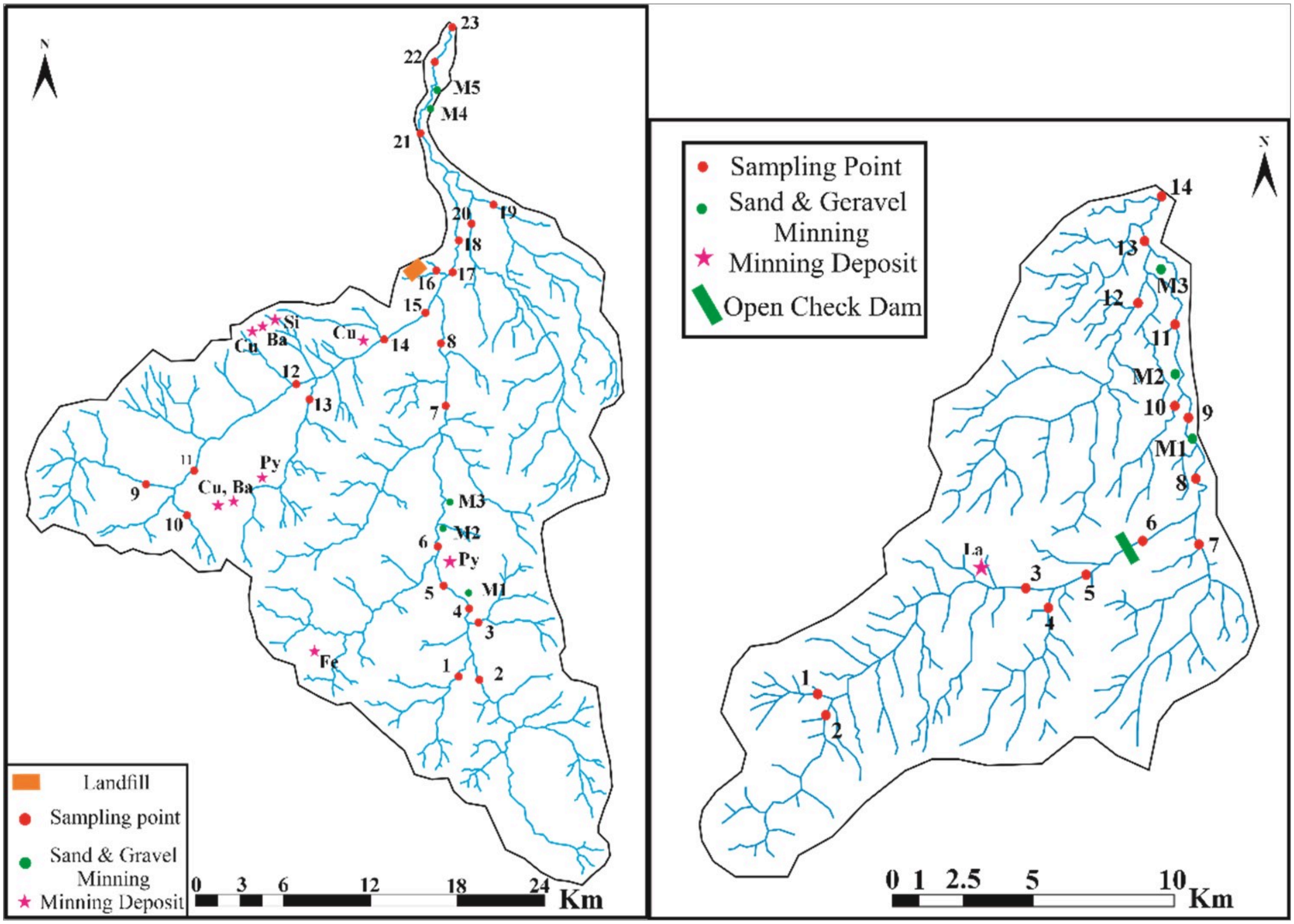

Figure 5

Locations of sampling stations.

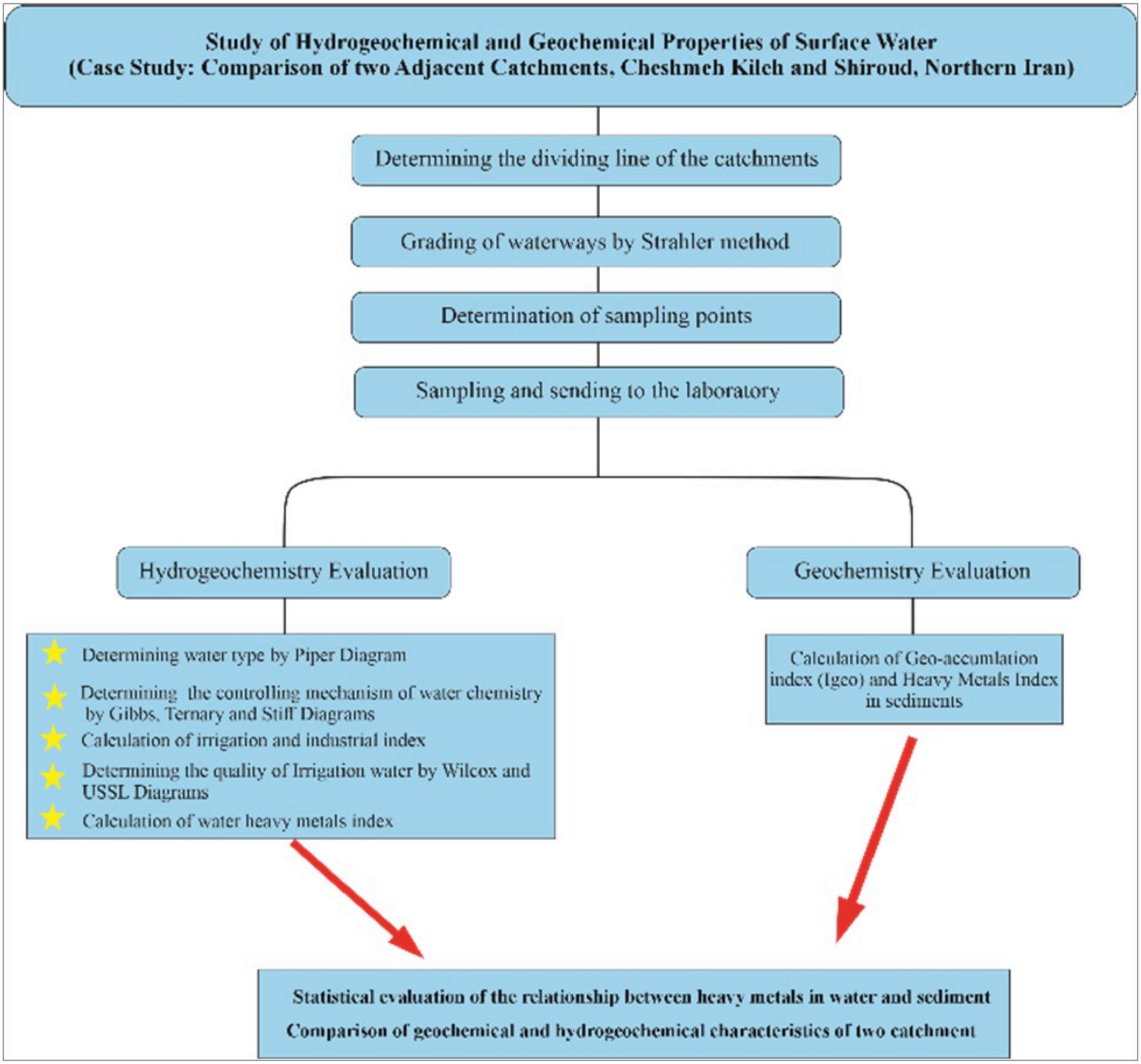

Figure 6

Chart of research method process.

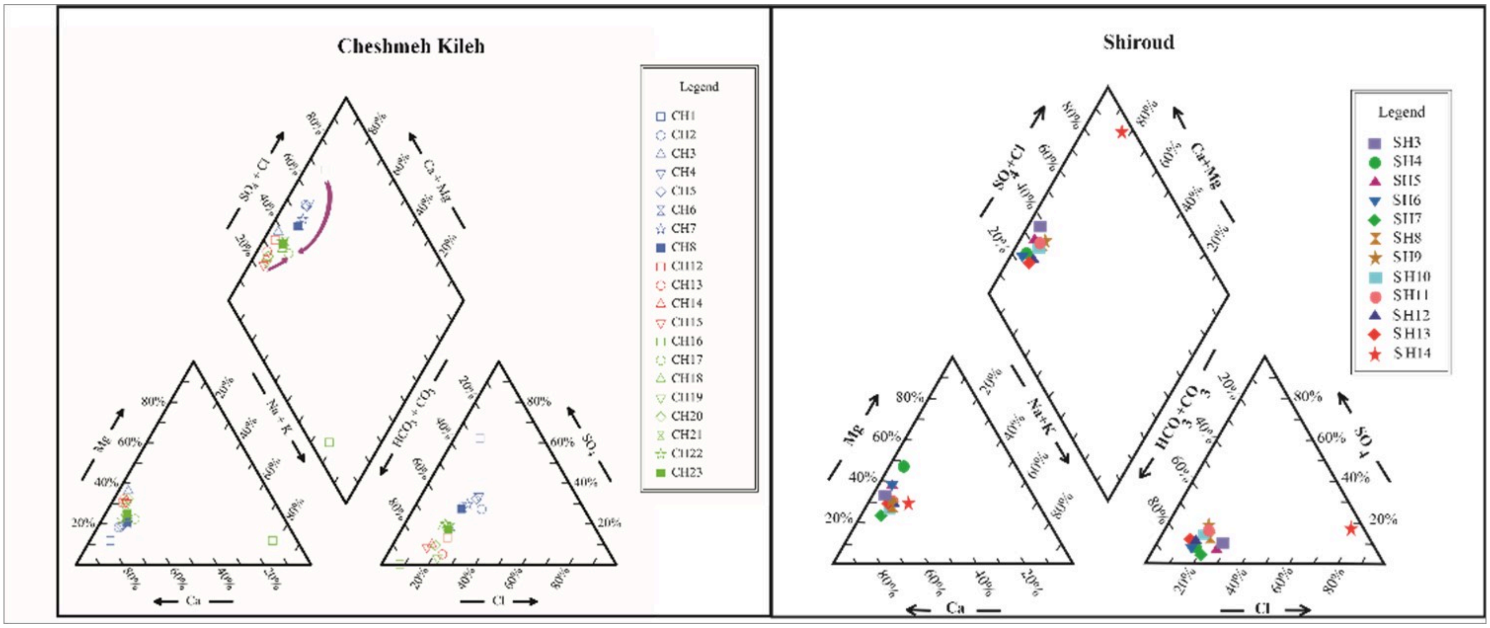

Figure 7

Piper diagram of Cheshmeh Kileh and Shiroud catchments.

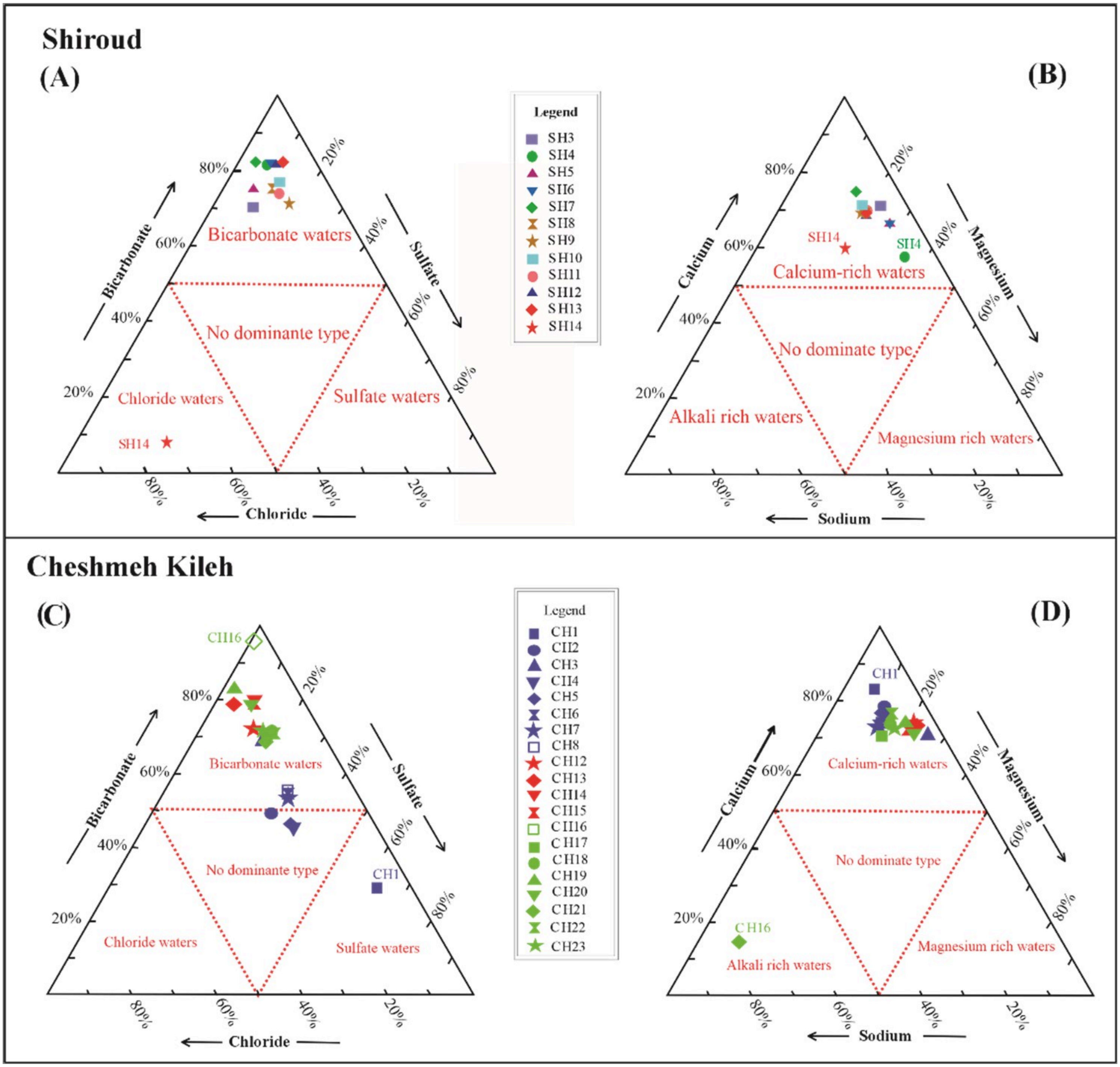

Figure 8

Ternary diagram of Cheshmeh Kileh and Shiroud catchments.

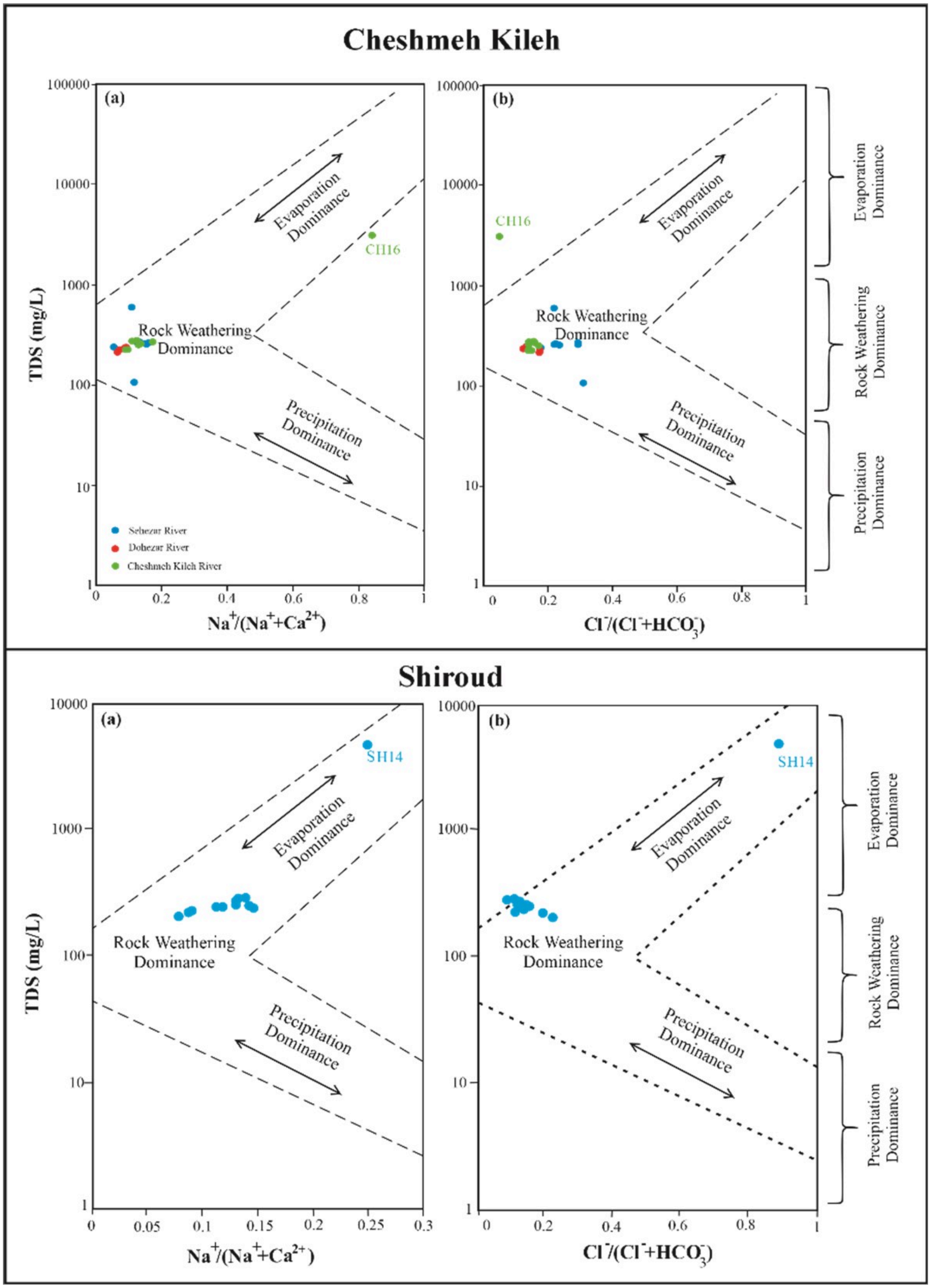

Figure 9

Gibbs diagram of Cheshmeh Kileh and Shiroud catchments.

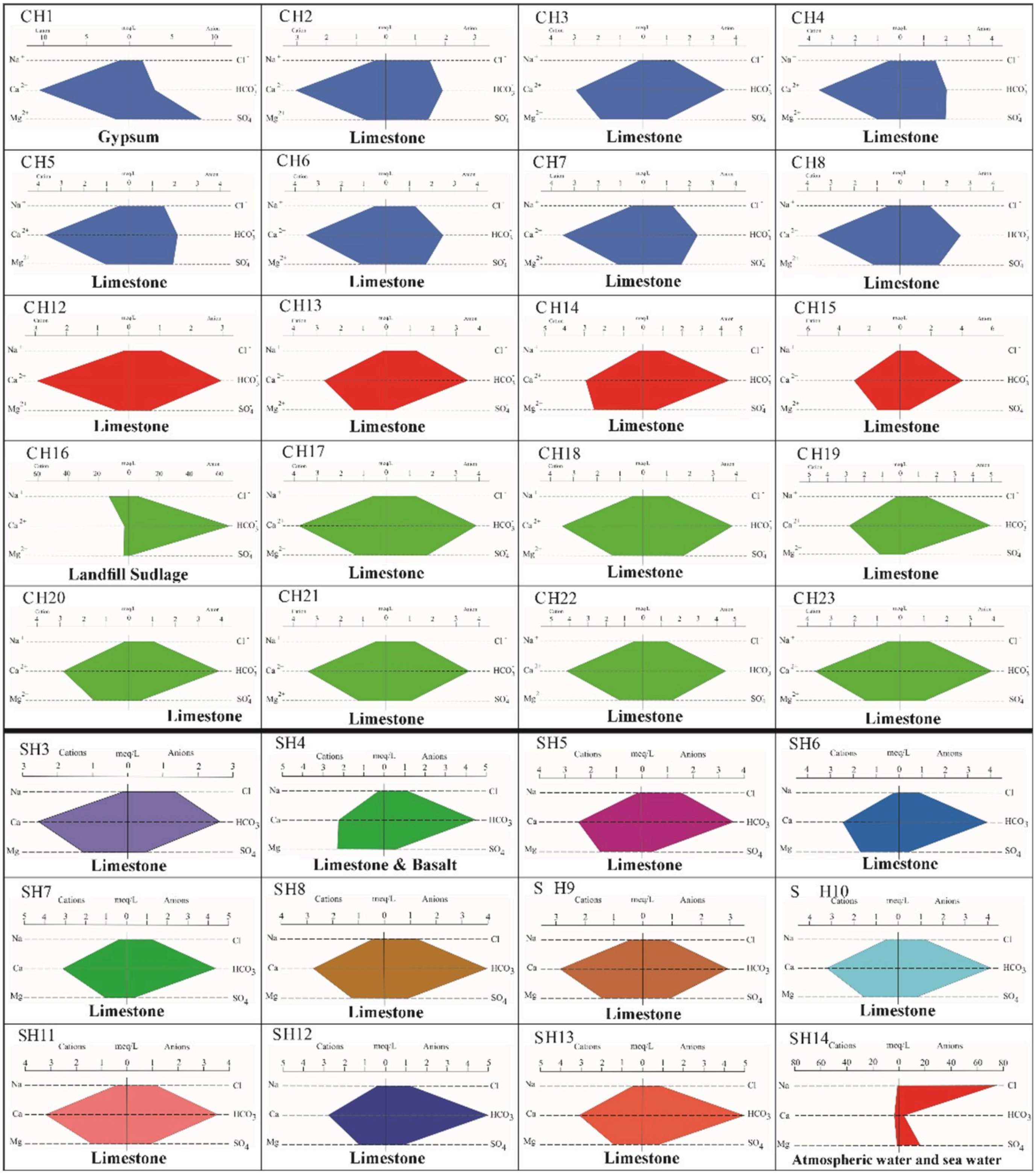

Figure 10

Stiff diagram of Cheshmeh Kileh and Shiroud catchments.

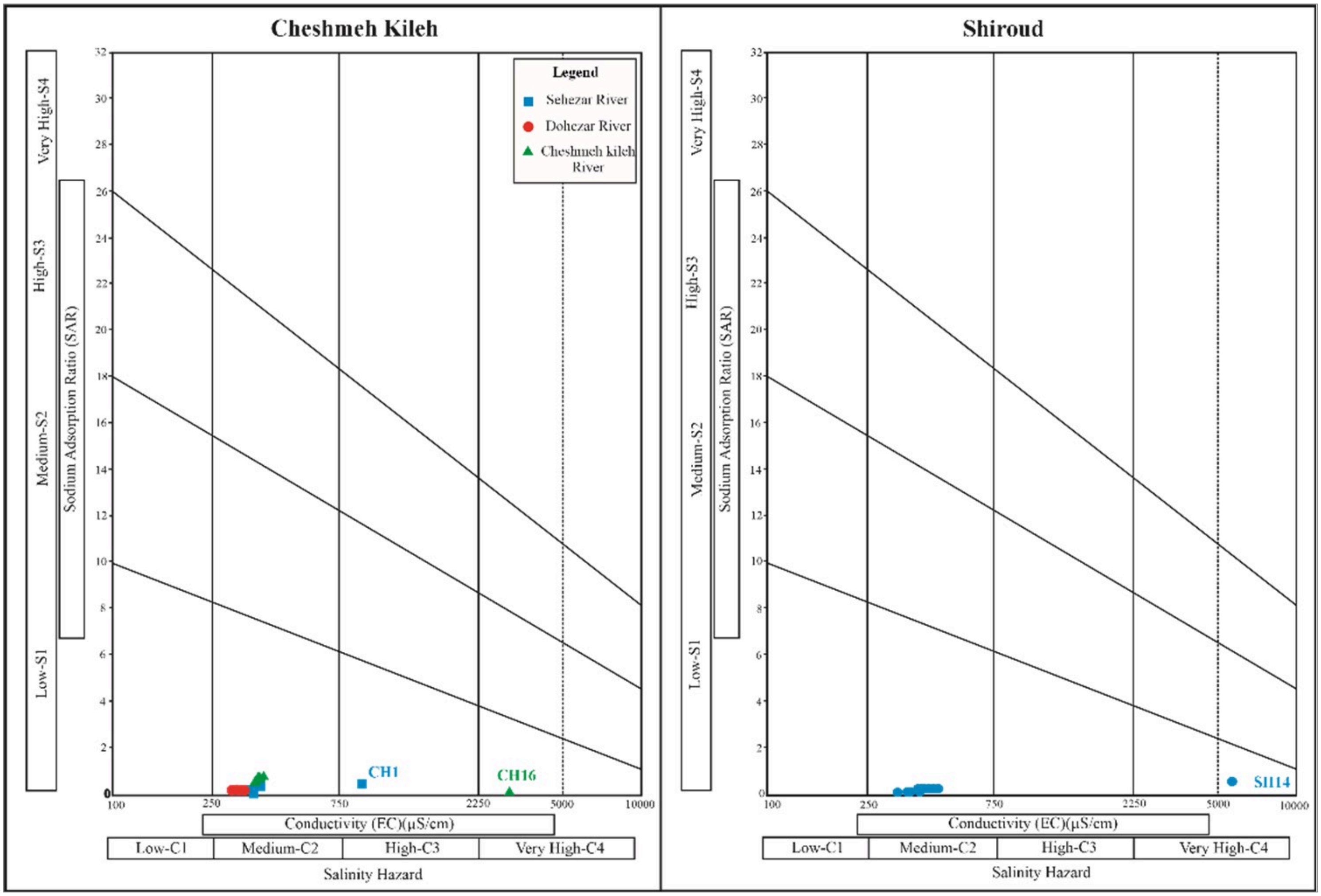

Figure 11

USSL diagram of Cheshmeh Kileh and Shiroud catchments.

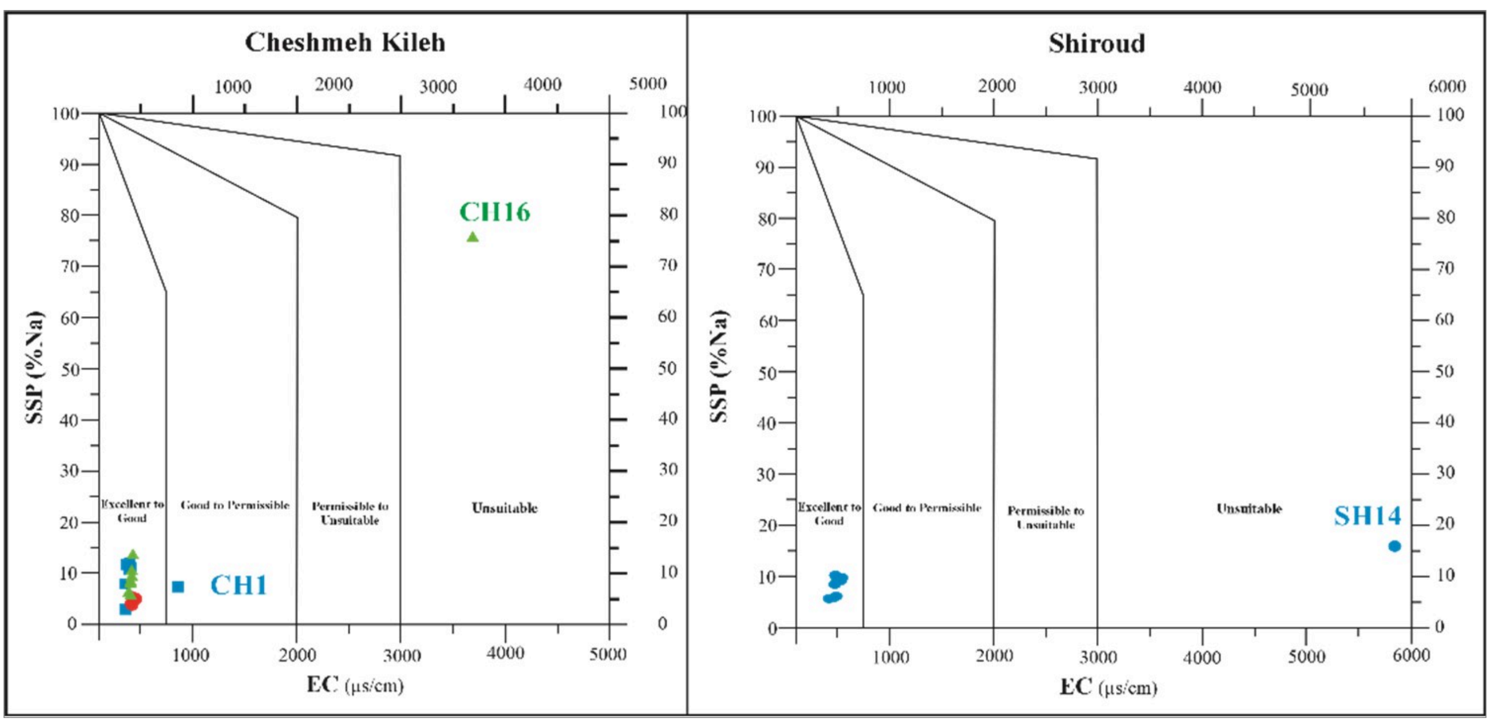

Figure 12

Wilcox diagram of Cheshmeh Kileh and Shiroud catchments.

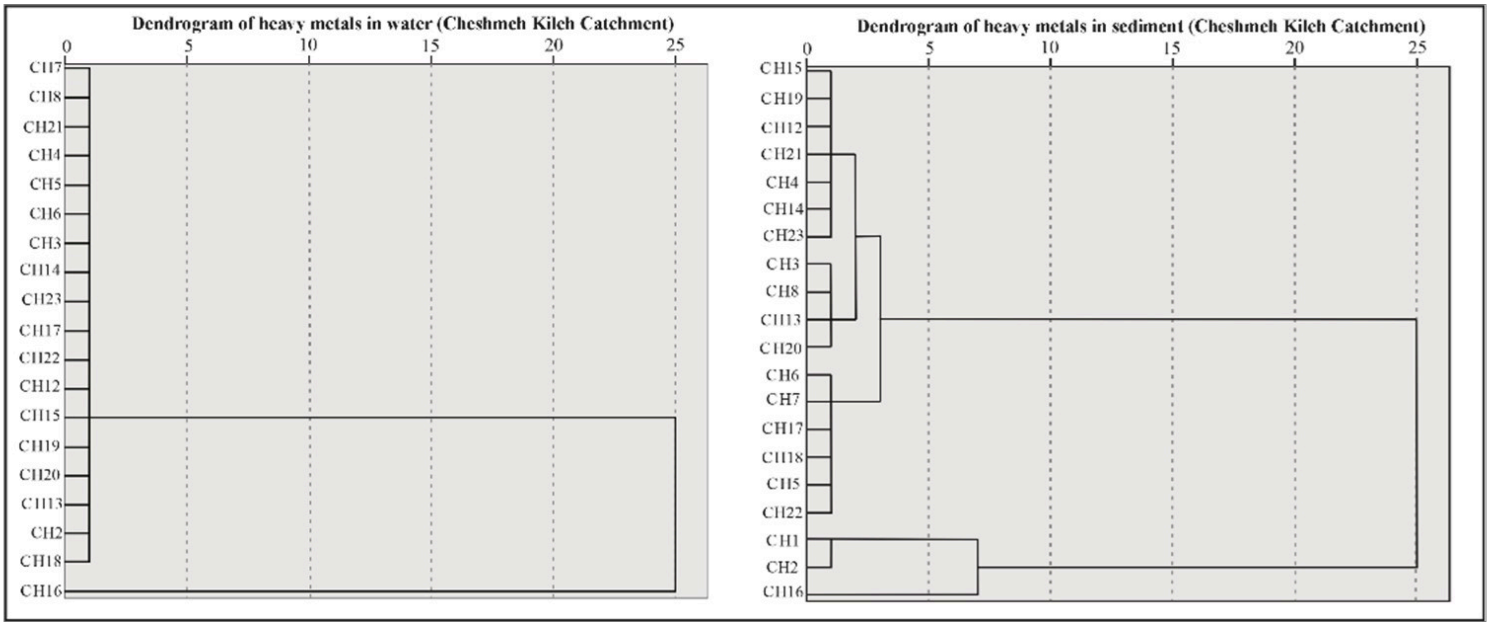

Figure 13

Hierarchical cluster analysis of heavy metal in Cheshmeh Kileh catchment, using dendrogram diagram.

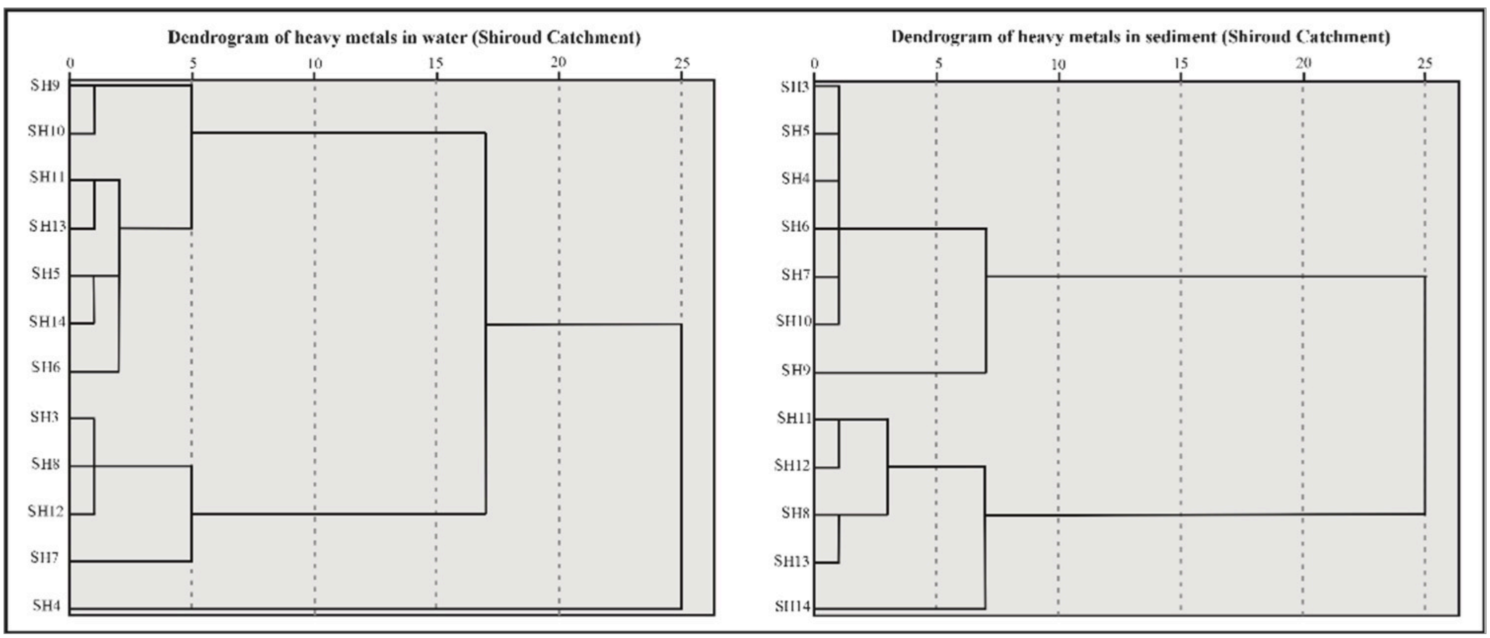

Figure 14

Hierarchical cluster analysis of heavy metal in Shiroud catchment, using dendrogram diagram.

Supplementary Files

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