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Major Ion Hydrochemistry of Niğde (Turkey) Plain Aquifer System

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Abstract Hydrogeochemical investigations are helpful for constructing the conceptual hydrogeologic model because hydrochemical properties of natural waters are results of some natural (precipitation/evaporation, water-rock interaction, and interaction of different water bodies) and anthropogenic processes (basically water use and land use for human need). In Turkey, particularly Central Anatolia groundwater is very important to water resource for human need (both agricultural, domestic and industrial usage as many other parts of the world. Beside the others, for many parts of Turkey, groundwater is an important water resource due to the insufficiency of surface water resources. In addition to its limited quantity, surface water resources have very poor quality.
26 groundwater and 2 surface water sample are collected from study area to understand the major hydrochemical properties. Physico-chemical parameters are measured in-situ and all samples are analyzed according to major ion. Results used to evaluate hydrogeochemical evaluation and groundwater quality of Niğde plain aquifer. According to results from interpretations, Niğde plain aquifer system is mainly affected by geological conditions. $Ca-HCO_3$ is the dominant water type due to fractured/karstic aquifer marbles recharge alluvium aquifer. While surface water pollution is very common, anthropogenic groundwater pollution is in subject where geological conditions let infiltration.

Keywords Groundwater, Niğde-Turkey, Alluvium Aquifer, Water Chemistry

Introduction

Water resources gain a very significant role haven't ever before play a more important role recently due to increasing population and industrial improvements. In addition to growing human population, improvements in technology, industry, and urbanization both water demand and negative effects on water resources are increased. Besides the amount of water, quality of water is more important for an area and style of water use. To understand these processes, hydrochemical properties of groundwater are widely used by researchers. Therefore, these properties of water resources are play a critical role for sustainable management of water resources and also for the sustainable development of the region. In Turkey, particularly Central Anatolia groundwater potential is very important for human needs such as agricultural, domestic and industrial usage. Additionally, hydrogeochemistry is very helpful in constructing the conceptual hydrogeologic model because the hydrochemical potential is very important for human needs such as agricultural, domestic and industrial usage. Additionally, hydrogeochemistry is very helpful in constructing the conceptual hydrogeologic model because hydrochemical properties of natural waters are the results of some natural (precipitation/evaporation, water-rock interaction, and interaction of different water bodies) and anthropogenic processes (basically water use and land use for human need) [1-3]. Beside the other significances, groundwater is an important water resource due to the insufficiency of surface water resources as one-third of total world population estimated by [4] and also for many parts of Turkey. This study is concerned about plain aquifer system around Niğde city center within

Central Anatolia, Turkey. Investigation area has a plain morphology which includes two industrial zones. One of them is a wastewater treatment center in Niğde city center and the other is some agricultural lands. As the geological structure is very complex in the study area, this situation increases the importance of understanding the hydrogeochemical properties of the study area. The study area hosts approximately 200K people and main water resource for all anthropogenic purposes is groundwater. For that reason, it is vital to determine hydrochemical characteristics of groundwater in the region. The aim of this study is to determine hydrogeochemical characteristics and to evaluate water quality and hydrogeochemical processes that affect the chemistry of groundwater in the region. Results from the study will also provide important data to evaluate chemical conditions of groundwater for anthropogenic purposes such as drinking and/or irrigation water quality.

For this aim, 26 groundwater and 2 surface water samples are collected from the study area from alluvium units limited by Akkaya Dam in the southeast. All samples are analyzed for the major ion. Analysis results are used to evaluate hydrogeochemical evaluation and groundwater quality of groundwater from Niğde city center alluvium aquifer system by using diagrams and standards.

Groundwater quality issue is very critical for domestic usage. Groundwater quality issue is very critical for domestic usage. Groundwater resources from urban areas are under risk in many areas in the world [5-7]. Many standards for some purposes are suggested by many researchers and institutions [8-10]. The results of hydrochemical investigations of this study compared with these standards to determine the quality class of water and obtain potential risks of usage.

Geological, Hydrogeologic and Climatic Setting

Niğde city is located in southeastern part of Central Anatolia. However Hasan, Melendiz, Aladağlar and Bolkar Mountains are in the border of Niğde city, the city center is located on Niğde Plain. (Figure 1). The study area is limited within this plain which hosts Karasu Creek. This creek discharges to Akkaya Dam Lake by passing through Niğde City. Creeks were generally dry during sampling period but after the wastewater treatment plant of Niğde Municipality taken into operation, it is flow rate seems relatively higher. It is observed that the creek is very polluted in this part of the study area.

Geological characteristics of the region is studied by many researchers [11-14]. The Niğde Plain which hosts Niğde city center extends in NW-SE direction. Metamorphic units of Paleozoic-Mesozoic outcrops in the eastern and southeast border of the plain. The basement of metamorphic rocks represented by gneiss and quartzites while uppermost units are represented by Aşıgediği marbles. Upper Cretaceous age metagabbros are located in the northwestern part of the study area. Melendiz volcanism affected the western and northwestern part of the study area and represented by andesites, basalts and pyroclastic rocks. Pliocene units are represented by terrestrial sediments but they have limited expansion. The main target of this study is Quaternary units which are composed of colluvial sediments and alluviums of Niğde Plain and represented by heterogeneously distributed gravel, sand, clay, and silt.

Groundwater resources are densely used for domestic, agricultural and industrial purposes due to the insufficiency of surface water resources. These circumstances rise the importance of hydrogeological characteristics of the region. The gneiss and quartzites of Niğde Massive basement units are impermeable while Aşıgediği Metamorphic rocks show permeable character due to their fractured structure. Also, metagabbros are impermeable. The agglomerates of Melendiz Volcanism are semi-permeable while basalts and andesites show permeable character due to their fractured structure. Pliocene formations are not important in hydrogeological mean because of their limited spread in the study area. The most important units by means of hydrogeology in the study area are Quaternary units which host many wells drilled for irrigation, domestic and industrial water needs. Quaternary units are permeable except clayed and silty levels. Quaternary units are permeable except clay and silt levels. It is noticeable that main groundwater flow direction is NE-GW according to investigations on wells and boreholes.

Surface water resources of the study are very limited. During sampling period (September 2016), the considerable flow could only be seen through Akkaya Dam Lake after wastewater treatment plant. Particularly, water pollution is in subject in the city center and industrial zones. Within city center, concrete channels are constructed by Niğde Municipality for Karasu Creek to disconnect creek and groundwater. A thermal water resource is discharging from an artesian well drilled by individuals for irrigation purposes. But the discharging water is not suitable for irrigation because it is thermal (27.3 $^{\circ}$C), blurred and enriched by sulfate which has rotten egg smell on well site. All surface waters, both natural (creeks) and anthropogenic (wastewaters from industrial zones and wastewater treatment center) recharge Akkaya Dam Lake. The water pollution is an environmental issue around Akkaya Dam Lake.

Continental climate conditions are dominant in the vicinity of Niğde. According to data from Turkish State Meteorological Service, the annual mean temperature is 11.2 $^{\circ}$C while minimum and maximum annual mean temperatures are 5 $^{\circ}$C, 17.5°C respectively. According to these data, the warmest season is July-August while coldest is January-February period. Total annual precipitation is 341 mm. The rainy months are April and May with 42.1 mm and 49 mm precipitation rates respectively while July and August are dry months with 4.5 mm, 5.5 mm precipitations.

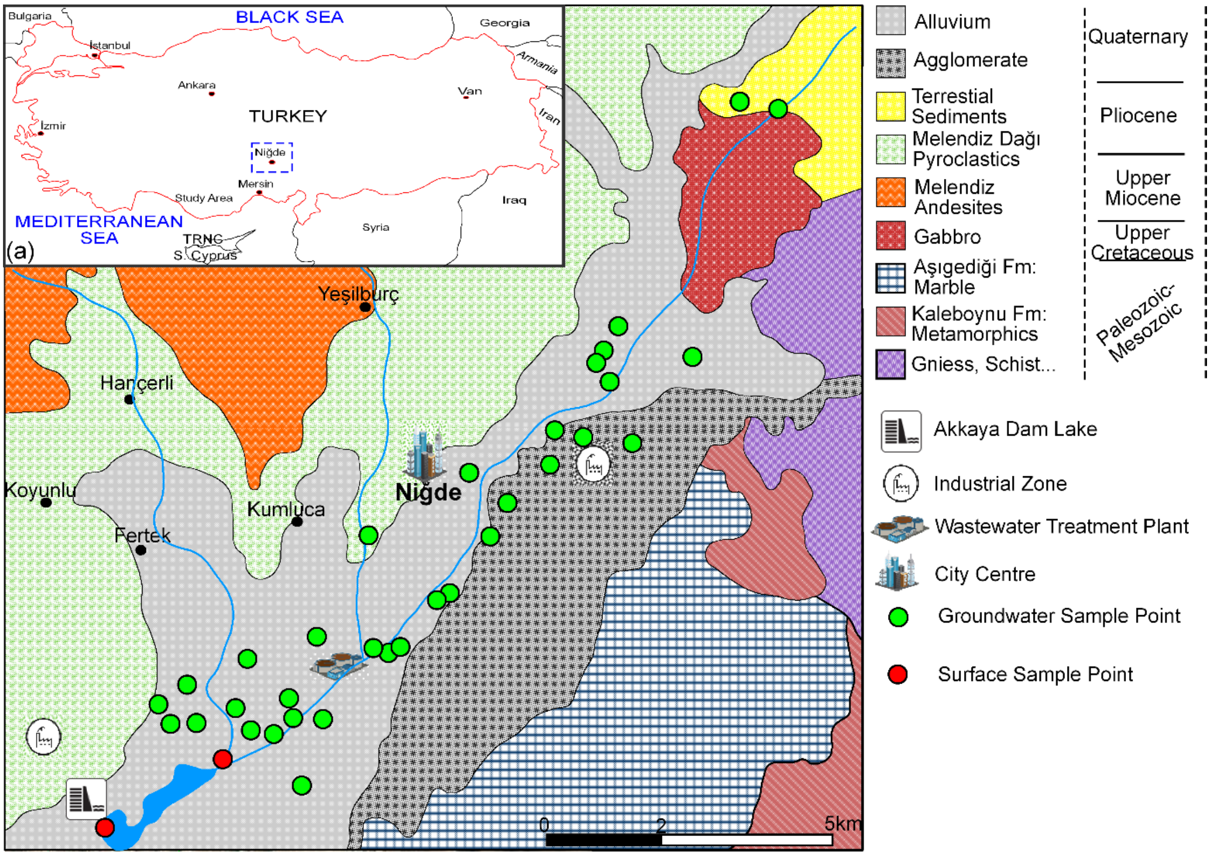

Figure 1: Location, geological and sample distribution map of the study area

Materials and Method

26 samples from wells and 2 samples from Akkaya Dam were gathered in September/2016 at the end of the dry season to determine hydrochemical behavior in the study area. In situ pH, temperature and electrical conductivity measurements were carried out by using Hach HQ 40d model Multi-analyzer. Samples collected in 250 ml double capped polyethylene bottles for major cation and trace element analyses and in 500 ml polyethylene bottles for anion analyses. Cation samples are acidified by pure HNO_3 to pH>2. All samples preserved at 4 °C prior to analyses. Major anion analyses are conducted at Analytical Chemistry Laboratories of General Directorate of Mineral Research and Exploration (M.T.A.) by using Ion Chromatography method except for HCO_3 by titrimetric method. Cation and trace element analyses are conducted by using ICP-OES device at Water Chemistry Laboratories of Earth Sciences Research and Application Center of Ankara University (YEBİM).

Results and Discussion

Physico-Chemical Parameters

For the aim of determination of hydrochemical properties of Niğde Plain alluvium aquifer, sampling studies conducted in September (2016). Simultaneously to sampling, physico-chemical parameters (pH, T, EC, DO, Eh) are measured in situ (Table 1).

Both temperature and pH are important parameters for interpretation of hydrochemical data. All samples are neutral with 6.3-7.84 pH values except 3 groundwater (5.67-5.92) and 1 sample from Akkaya Dam Lake (8.11). Temperature of groundwater provides lots of information about thermal water intrusion to the freshwater aquifer and/or circulation depth of groundwater and chemical reactions occurred in aquifer [3]. According to measured values, the temperature of groundwater samples vary between 14-20 °C while discharge temperature of artesian well water sample 20 is 27 °C (Table 1). Rotten egg smell is present at this well site where white and blurry groundwater discharges. [15] defined waters as hypothermal which discharge temperatures are between 20-30 °C. Discharge temperature of sample 22 is also above seasonal mean atmospheric temperature. According to its discharge temperature sample, 22 is defined as thermal water. Temperatures of surface waters are sampled at 19 °C for creek sample from just before Akkaya Dam Lake and 16 °C for Akkaya Dam lake sample. As seen in Table 1, creek water is hotter than Akkaya Dam Lake sample because wastewater treatment plant is recharged Karasu Creek in this region. Water temperature will be balanced in Akkaya Dam Lake with atmospheric temperature in time.

EC values of water is a result of total dissolved ions in water. In the study area, EC values are between 387-1472 µS/cm. It is clear from site distribution of samples EC values increases through the center of plain and especially in the vicinity of thermal water (sample 20). EC values of surface waters are 996 and 1138 µS/cm due to heavy pollution rises from domestic and industrial pollution.

Table 1: Results of physico-chemical measurements and chemical analyses

No	**pH**	**Eh**	**DO**		**EC**	**TDS**	**T**	**Ca^{+2}**	**Mg^{+2}**	**Na^{+}**	**K^{+}**	**HCO_3^{-}**	**SO_4^{-2}**	**Cl^{-}**
		mV	**mg/l**	**%**	**µS/cm**	**mg/l**	**°C**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
SK1	6.32		6.89	81.8	637	426.79	17.2	104	25	31	12	345	87	11
SK2	6.62	22.5	0.44	110	515	345.05	16.3	98	17	26	10	397	23	10
SK3	6.37		6.89	86.5	488	326.96	19	75	17	28	10	298	29	12
SK4	6.62		5.1	58.8	831	556.77	15.7	159	27	38	10	397	180	18
SK5	6.96	3.4	5.45	63.5	660	442.2	16.3	97	25	28	11	429	25	13
SK6	7.16	-7.7	6.73	76.8	766	513.22	15.6	146	26	27	12	532	24	11
SK7	6.73	16.1	3.7	43	1020	683.4	16.1	134	24	42	15	286	99	98
SK8	6.81	11.5	4.17	48.5	955	639.85	16.1	138	22	40	14	280	105	91
SK10	6.57	25.3	1.93	23.1	813	544.71	17.5	130	19	42	13	356	115	29
SK11	7.52	-27.6	8.3	94.9	460	308.2	14.4	44	7	8	3	134	36	7
SK12	6.3	40.4	6.89	83	532	356.44	17.3	90	16	23	9	350	11	7
SK13	7.84	-46.9	7.64	106.7	394	263.98	19	58	13	19	4	222	16	10
SK14	6.47	30.2	5.51	63.5	529	354.43	15.5	87	15	23	6	339	22	11
SK15	7.07	-3	2	23.1	1074	719.58	15.1	187	32	51	16	590	141	47
SK16	5.87	64.7	3.02	37.7	772	517.24	19	134	24	47	16	239	287	17
SK17	5.92	61.2	2	23.4	812	544.04	16.3	145	27	50	18	264	280	17
SK18	6.56		3.1	35.5	1147	768.49	15.6	206	50	43	18	547	287	24
SK19	7.19		6.69	77	761	509.87	15.5	144	31	37	11	481	83	22
SK20	6.69		1.87	21.2	1472	986.24	15.2	344	59	45	18	375	698	28
SK21	7.5	26.7	7.68	89.9	387	259.29	16	59	17	12	5	252	18	9
SK22	5.67	78.2	1.86	27	701	469.67	27.3	167	19	19	17	237	299	14

SK23	7.11	-5	5.21	59.2	781	523.27	14.2	149	19	20	4	433	74	26
SK24	7.32	-16.9	1.04	12.7	969	649.23	18.8	152	10	134	16	650	2	74
SK25	7.06	-37.7	4.19	50.8	856	573.52	18.6	170	27	36	8	629	10	22
SK26	8.11	-61.2	0.39	4.6	1138	762.46	15.5	121	19	82	25	515	43	87
SK28	7.15	-7.3	5.63	69.2	412	276.04	16.5	71	15	16	7	202	60	24
SK31	6.98	2.1	6.73	87	437	292.79	15.3	90	13	23	8	176	160	7
SK32	7.48	-25.6	6.9	83.4	406	272.02	15.4	71	22	17	9	287	32	10

Major Ion Chemistry

Major Ion chemistry of groundwater is a very useful tool for understanding groundwater compositions and hydrochemical types of groundwater. Hydrochemical properties of groundwater mostly reflect the composition of mineralogical and thermodynamical conditions. Thus, hydrogeochemical investigations are the most useful tools for understanding the processes that efects water quality along the flow path. Major ion chemistry data is presented in Table 1. One of the most useful tools for the evaluation of hydrochemical data is to introduce them with some diagrams. With this aim, many researchers suggest some diagrams [16-18]. Piper and Schoeller diagrams are the most used diagrams by researchers to understand the main hydrochemical properties and types of waters. According to distribution and pattern of samples on Scholler plot (Fig 2) mainly 3 different characters is obtained. The first hydrochemical type is the most dominant type which is enriched by Ca among cations and HCO_3 among anions. The secondly dominant type is $Ca\text{-}SO_4$ type waters and the third one is surface waters by their relatively enriched Na+K concentrations.

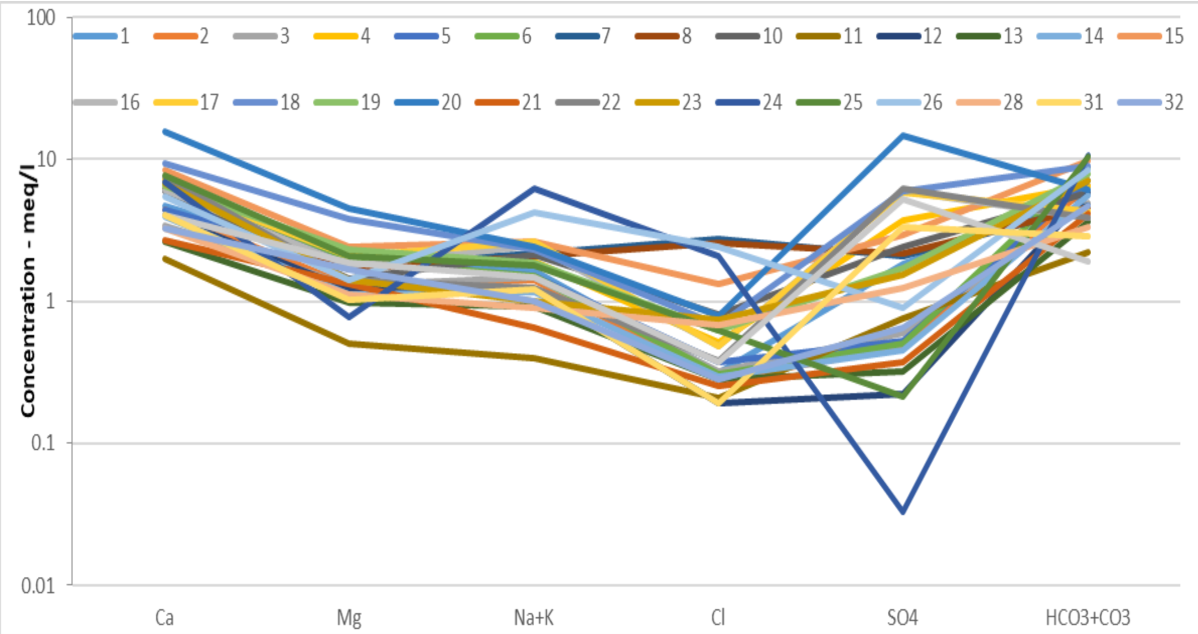

Figure 2: Schoeller plot of samples from the study area

It can be seen from Piper plot (Fig 3), main water type of samples from Niğde Plain is $Ca\text{-}HCO_3$, however, some samples plotted on $Ca\text{-}SO_4$ area. From the diagrams, it is obtained that sample 22 is most enriched water by SO_4 and samples in the vicinity of sample 22 are also enriched by SO_4 relative to others. Sample 22 is defined as thermal water due to its discharge temperature of 27 °C and both rotten egg smell and sulfate depositions are present along the artesian well site.

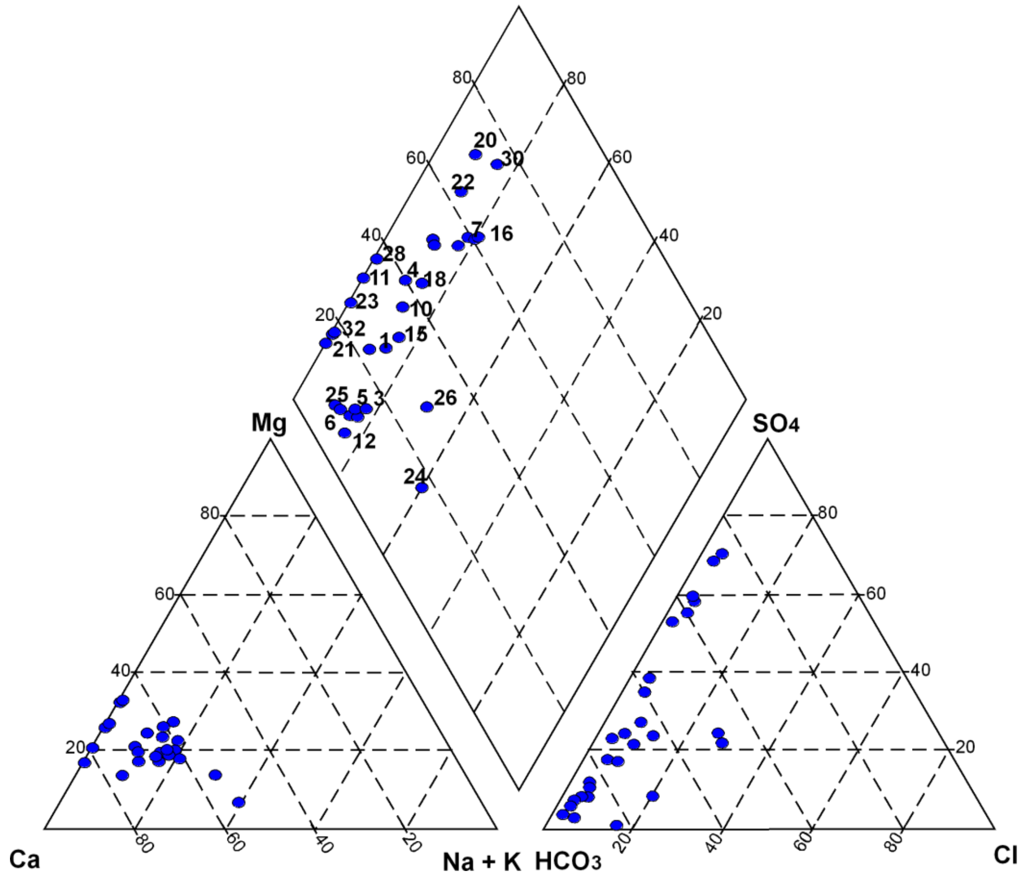

Figure 3: Piper plot of samples from the study area

Another diagram used to evaluate the hydrochemical data is Gibbs diagram (1970) which dominant processes that the hydrochemical properties of waters are affected. On this diagram, it is clear that the main chemical process that affected the water chemistry is water-rock interaction rather than evaporation or precipitation.

Interpretations of diagrams show that hydrochemistry of Niğde Plan Aquifer system is mainly controlled by the geological structure of the study area. The metamorphic rocks at the basement of the study area limit the plan from its eastern border. It is concluded that fractured/karstic aquifer of Aşıgediği marbles at the uppermost part of the metamorphic rocks recharges alluvium aquifer with the Ca-HCO_3 type of water. It is obtained that some wells are drilled into Melendiz Volcanics in the western part of the study area. The hydrochemical type of groundwater samples from this well is Ca-HCO_3 too.

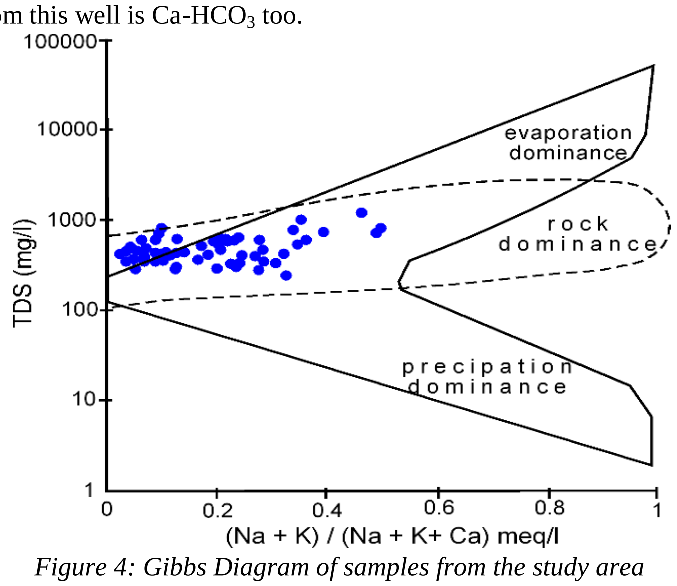

Figure 4: Gibbs Diagram of samples from the study area

In the vicinity of the well (Sample 20) which discharges thermal water all ion concentrations, particularly SO_4 and EC values are enriched. Water type of groundwater changed to Ca-SO4 in this region. In the near vicinity of the study are there is no lithological unit to explain the Ca-SO_4 dominant character of groundwater. This strengthened the possibility of thermal water intrusion form a fractured zone to the alluvium aquifer.

Any relation between ground and surface water resources can not be detected in the vicinity of Akkaya Dam Lake. The reason of this is the blockage of the filtration by deposited clayed and silty sediments. The enrichment of Na and K concentrations of surface water samples (sample no 24 and 26) relative to groundwater samples depends on clayed and silty units deposited in this region and fine-grained sediment load of Karasu River. Increases in EC values of surface water samples are related to pollution.

Water Quality

Groundwater use for domestic, agricultural and industrial purposes is very common in the region due to the insufficiency of surface water resources by means of both quality and quantity. Quality of water is particularly important for groundwater use for domestic purposes. Water quality parameters and limits according to common standards [8-10] are presented in Table 2.

pH of 3 samples from the study area is lower than all standard values (pH<6) and classified as Class 4 according to WPCR. EC values of samples are between 387-1472 µS/cm and out of limit value suggested by WHO but in the permissible limit of EPA. All samples from the study are classified as Class 1 and 2 according to their TDS concentrations (WPCR) and they exceed the limit of EPA (1993) with 14 sample. DO concentrations are distributed to Class 1, 2 and 3 but 7 samples are classified as Class 4 (WPRC). Na, Cl concentrations are in limits but Na concentrations of surface water samples are out of limits for WPCR Class 1 and 2. SO_4 concentrations are out of limits in the vicinity of thermal water well.

Table 2: Comparison of water quality data with standards

	WPRC (2004)				WHO (1998)	EPA (1998)	Study Area
	I	II	III	IV	MAC	MAC	Min-Max
pH	6.5-8.5	6.5-8.5	6.0-9.0	<6,>9	6.5-8.5	6.5-9.5	5.67-8.94
EC (µS/cm)					250	2500	387 -1472
TDS (mg/l)	500	1500	5000	>5000	1000	500	259.3-986.2
DO (mg/l)	8	6	3	<3			0.39-9.37
Na (mg/l)	125	125	250	>250	200	200	7.6-134
Cl (mg/l)	25	200	400	>400	250	250	6.74-97.5
SO_4 (mg/l)	200	200	400	>400	250	250	2-698

Results from water quality interpretations show that surface water quality is too low according to Na. For groundwater samples parameters pH, DO, EC, TDS, and SO_4 are out of permissible limits. And it is concluded that water quality is under control of geological and hydrogeological conditions and thermal water intrusion (EC, TDS, SO_4). To have a detail look at water quality of water resources in Niğde Plain, it is strongly suggested that to analyze samples according to other pollution parameters such as toxic components (NO_3, PO_4 NO_2, NH_4, B, As, Mn, Cu, Al…).

Conclusion

The main process that obtains groundwater chemistry in Niğde Plain is water-rock interaction. Hydrochemistry of Niğde Plain aquifer is dominated by the Ca-HCO_3 type of water although the Ca-SO_4 type is in the subject through the southern part of the study area which thermal water discharges from an artesian well. It is concluded that Ca-HCO_3 type is due to fractured/karstic aquifer of Aşıgediği marbles is hydraulically connected with alluvium aquifer and recharges it. However, the geological setting of Niğde Plain and it is neighborhood can't explain this type of water due to no evaporitic unit is determined/reported. Therefore it is concluded that thermal water is discharging from a covered fracture zone. Control of geological structure can be seen on surface water chemistry with increases on Na values of surface water samples relative to groundwater due to the clayed and silty structure of Akkaya Dam Lake region and fine grain sediment load of Karasu Creek.

Results from water quality interpretations show that surface water quality is too low according to Na. For groundwater samples parameters pH, DO, EC, TDS, and SO_4 are out of permissible limits.

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