

Hydrogeochemical Characteristics and Groundwater Quality Assessment of a Relatively-Pristine Agricultural Basin (Palas Basin)

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ABSTRACT. This study investigates the spatial and temporal changes in groundwater levels and quality in the Palas Basin, a relatively-pristine semi-arid agricultural basin in Türkiye. Although groundwater is solely used as irrigation and drinkingpotable water resource throughout the basin, measurements regarding the dynamics and quality of groundwater were quite rare. The analyses were based on data collected from 12 water quality monitoring wells and 15 groundwater level monitoring wells during June 2019-May 2020. Water samples were analyzed for pH, electrical conductivity, temperature, nitrate, nitrite, ammonium, total nitrogen, total hardness, alkalinity, chloride, sulfate, phosphate, total organic carbon, calcium, magnesium, sodium, potassium, and arsenic. Data analyses included hydrogeochemical analysis and multivariate statistical analysis such as principal component analysis and cluster analyses. Results showed that water quality in the basin is mostly controlled by natural factors, however, anthropogenic impacts from agriculture activities were apparent in some regions. The basin shows significant changes in water levels throughout the year due to irrigation activities. The groundwater quality was classified as either Ca-Mg-HCO₃ and Ca-Mg-SO₄ type. In the majority of the basin, water quality was suitable for irrigation and drinking water uses, however, a few sampling sites had very high electrical conductivity, sulfate, nitrate, and arsenic levels. The high levels of nitrates were detected in areas, where agriculture is intense, indicating that agricultural activities might be affecting water quality. High sulfate, electrical conductivity, and arsenic levels could be related to the hydrogeological setting of the basin. This study showed that agricultural activities and natural factors were effective on the hydrogeochemical characteristics of the Palas Basin.

Keywords: Groundwater Quality, Groundwater Levels, Agriculture, Palas Basin

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1. INTRODUCTION

Groundwater is an important resource, used for meeting municipal, industrial, and agricultural water requirements, particularly when surface water resources are limited [1, 2]. The pressure on groundwater resources increases everyday due to population growth, industrial development, and agricultural intensification [3, 4]. Overexploitation and water quality deterioration are two important problems that threaten the sustainability of groundwater systems.

Groundwater is used extensively worldwide for meeting agricultural water requirements. On the global basis, the total area irrigated by groundwater is estimated to be 98 million ha or 39% of total irrigated area [5]. The amount of groundwater use is estimated to be 545 km³ yr⁻¹ [5]. As large amounts of water are extracted for irrigation, groundwater level and quality changes have been detected in many previous studies [6-8]. With the climatic changes, the pressure on groundwater systems is expected to become more apparent [6].

In this study, we collected data from a relatively pristine agricultural basin in Türkiye (Palas Basin) and analyzed the groundwater level and quality data to investigate hydrogeochemical characteristics of groundwater and spatial and temporal changes in groundwater levels and quality. In Türkiye, groundwater is used as the water resource at about 49% of total irrigated area [5]. Surface water and groundwater use in all sectors was estimated to be 54 billion $m^3 yr^{-1}$ [9]. The amount of groundwater use in the agricultural sector was estimated as 9.8 billion m³ yr⁻¹ [9] and 9.3 billion $m^3 yr^{-1}$ [5] by two different studies. Groundwater use is particularly important for agriculture in the semi-arid Central Anatolia region, as surface water resources are comparatively limited than other regions. Changes in groundwater levels has received significant attention in Türkiye in recent years. Downward trends in groundwater levels have been reported in different basins [10-12]. Despite strong interest in groundwater level declines, groundwater quality changes and the relationship of these changes with agricultural activities have not been sufficiently explored. Most of the basins, examined in earlier studies, were under a number of stress factors (such

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as population growth, urbanization, etc.) and the relationships of water quality with agricultural activities could not be clearly established.

The main purpose of this study is to evaluate the spatial and temporal changes in groundwater levels and quality in the Palas Basin. Groundwater is used as drinking and irrigation water in the Palas Basin, where agricultural activities are common and surface waters are insufficient. There are no large cities and almost no industrial activity in the basin, therefore agriculture can be considered as one of the major drivers for groundwater quality and level changes. This study may provide insights for understanding the linkage between the agricultural activities and groundwater systems in semi-arid regions.

2. MATERIALS AND METHODS

2.1 Study Area

The study area, Palas Basin, is located in the Kayseri province, in the Central Anatolia region of Türkiye (Fig. 1). The basin is located at 1135 m (asl) altitude and has a drainage area of 480 km² [13]. Palas Basin, which has the characteristics of a sedimentary basin, is surrounded by hills with relative elevation differences of 300-400 m. With this feature, it is a closed basin. The central basin has a relatively low slope and the basin topography extends from east to west. Tuzla Lake is a shallow saline lake with an altitude of 1131 m, located to the northwest of the basin. Tuzla Lake, which has a length of about 8 km and a width of about 4 km, has a surface area of 35 km². The lake is fed by Değirmen River, springs, and groundwater [12].



Fig. 1. Location and geographic characteristics of the Palas Basin

The study area has a semi-arid climate. Therefore, the summer months are hot and dry and it is quite cold and snowy in the winter. Average annual temperature in the region is 10.6°C (based on the 1975-2018 period). Most of the precipitation occurs in winter and spring. The average annual precipitation is 411 mm (1975-2018 average).

Geological formations in the Palas Basin can be divided into three main groups. These are Quaternary alluviums in the lake and its immediate surroundings, Tertiary-aged formations spread over a wide area in the east of the basin, and Mesozoic formations located in a narrow area in the southwest of the basin (Fig. 2). Palas Basin was formed by the filling of the quartz-aged alluvium that collapsed as a result of faulting. The oldest units in the basin are Mesozoic units and they cover an area of approximately 33 km², in the southwestern part of the basin. The mountains surrounding the west of the basin are composed of ophiolitic series and these series consist of marly, sandy, and calcareous rocks with conglomerates in some places. Ophiolites in the southern mountains contain large serpentine blocks and are found in volcanics such as diorite and gabbro. Tertiary formations spread over a wide area in the east and south of the basin. Eocene flysch covers 210 km² of the basin, while neogene basalts, volcanics, unallocated terrestrial sediments, and conglomerates cover an area of approximately 52 km². Quaternary formations are the youngest units in the basin. They cover an area of approximately 148 km² around Tuzla Lake (Fig. 2).



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Fig. 2. Geological and land use/cover characteristics of the Palas Basin

Agriculture is the major economic activity in the study area. 60% of the basin is used as agricultural land [13](Fig. 2). Due to its distance from the city center, industry has not developed in the region. Palas Basin land cover was obtained from the CORINE 2018 database. A large part of the basin covers non-irrigated arable lands (39%), sparse vegetation (27%) and continuously irrigated areas (15%). Other important land cover classes include natural meadows (5.5%) and areas with natural vegetation (4%). Palas Lake covers about 2% of the basin. Azgin and Dadaser-Celik [14] observed that irrigated agriculture intensified in the region, which caused further decrease in surface water flows. In another study, the changes in water levels of Tuzla Lake (Kayseri) were found to be related to groundwater level decreases [13]. The susceptibility of groundwater levels to irrigation was investigated using a groundwater flow model [12, 15]. To the best of our knowledge, no extensive analysis on groundwater quality is

in the study area. For this purpose, 12 water quality

sampling wells were selected considering the locations of

settlements and agricultural areas in the region (Fig. 3a). 15 sampling wells were used for monitoring groundwater levels (Fig. 3b). In order to monitor the spatial changes in groundwater quality as well as the temporal changes,

samples were collected monthly from June 2019 to May

available for the basin. This is very important research gap for a basin where groundwater provides the only water resource for drinking and irrigation uses.

2.2 Sample Collection and Field and Laboratory Studies

A groundwater sampling campaign was designed to determine the groundwater quality and groundwater levels



2020.

Fig. 3. Groundwater level (a) and quality (b) sampling points

Analyses for pH, electrical conductivity, temperature, nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺), total nitrogen (TN), total hardness, alkalinity, chloride (Cl⁻), sulfate (SO₄²⁻), phosphate (PO₄⁻³), and total organic carbon (TOC) were performed monthly. Seasonal analyses were conducted for calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), and arsenic (As³⁺) (May 2019, July 2019, September 2019, and January/February 2020). pH, temperature, and electrical conductivity were measured onsite using Hach Lange HQ-40D multimeter. For other analyses, samples were transported to the laboratory and stored in the refrigerator at +4°C until the analysis was done. Nitrate (EN 38405 D-2), ammonium (ISO 7150-1), total nitrogen (EN ISO 11905-1), phosphate (EN ISO 6878), and sulfate (Extinction/Turbidimetric) analyses were conducted using spectrophotometric methods using Hack Lange cuvette tests. Alkalinity (SM 2320 B), hardness (SM 2340 C), and chloride (SM 4500- C1 B) were measured by titration. Calcium, magnesium, potassium, sodium, and arsenic were measured using an ICP-MS Device, while TOC was measured using a Shimadzu TOC-L CPN device.

2.3 Data Analyses

The collected water level data were used to identify seasonal changes in groundwater levels. These data were also used to identify groundwater flow direction in the center alluvial aquifer system.

Water quality data were first analyzed for seasonal variations. We also evaluated the suitability of groundwater for municipal and irrigation uses by comparing the values with limit values set by World Health Organization (WHO). Piper diagram was prepared for understanding the characteristics of the groundwater in the basin. SAR diagram was used to evaluate the suitability of waters for irrigation. We applied multivariate statistical techniques for analyzing water quality data. Principal component analysis is a data transformation technique that converts multivariate data sets into fewer data sets, namely basic components (PC), by capturing their basic characteristics [16]. The PCs obtained rank the variation from high to low. Cluster analysis was used for grouping sampling sites with similar characteristics [17]. Hierarchical clustering analysis is the combination of clusters according to their similarity or distance (Euclid, Euclidin square, Manhattan distance, etc.) values. Dendogram is a commonly used representation. Each unit in the dendogram represents a cluster and the two closest units combine to form another cluster.

3. RESULTS AND DISCUSSION

3.1 Water Level Changes

Groundwater levels were monitored at 15 wells between June 2019 and May 2020 in the Palas Basin (Fig. 3a). We developed a map (Fig. 4) to show average groundwater levels in the region during the analysis period. In this analysis, we focused on the alluvium aquifer in the central basin, due to the presence of comparatively higher number of sampling wells in this region. As can be seen groundwater flows from southeast to the northwest and discharges in to Tuzla Lake as documented by previous studies [12].

We investigated the seasonal changes in groundwater levels from June 2019 to May 2020 (Fig. 5). The lowest value in the groundwater levels in the study area is the S8 sampling well, located at 47.5 m at 1174 m in the northeast of the basin. It was observed that groundwater levels at the majority of the wells went down during the summer and autumn seasons. The decrease in water levels could be clearly identified in sampling wells S5 and S15, which are located in the area where irrigated agriculture is concentrated. It was observed that water levels increased in the entire basin following precipitation in the winter and spring seasons.



Fig. 4. Average groundwater elevations (m) during the June 2019-May 2020 period



Fig. 5. Seasonal changes in groundwater levels during the June 2019-May 2020 period

3.2 Hydrogeochemical Characteristics and Suitability of Groundwater for Drinking Water Uses

Groundwater quality varies as a result of natural factors as well as anthropogenic activities [4, 18, 19]. The hydrogeochemical characteristics of groundwater are related to the soil/bedrock material, the residence time in the aquifer, and biological and chemical processes [20]. Investigating the chemical composition of groundwater can improve our understanding of these processes and help identify the sources of pollution [21, 22]. Averages of monthly measurements collected in the Palas Basin are given in Table 1. Spatial distribution of average values is given in Fig. 6. The suitability of groundwater quality as drinking water was evaluated according to the limit values set by the World Health Organization (WHO).

Table 1. Average	groundwater quali	tv values (.	June 2019 - Ma	v 2020)	(BL: below	detection limit)
rable rentronge	Stoulla water qual	ty values (June 2017 1010	, 2020,		detection minity

Sample No	K1	K2	K3	K4	K5	K6	K7	K8	K9	K10	K11	K12
Temperature (°C)	18.2	16.5	16.5	14.2	14.9	17.1	17	22.5	16.2	16.8	17.2	17.9
pH	8.2	7.8	8.2	7.9	7.9	8.1	8	8.1	8	8.2	8.1	8.1
Electrical Conductivity (µs/cm)	1009	1757	1681	714	666	388	350	570	461	558	371	2134
Nitrate (mg/L)	18	18	17	59	65	9	10	21	15	27	11	26
Ammomium (mg/L)	0.2	0.1	0.1	0.1	0.1	0.05	0.1	0.2	0.1	0.2	0.4	0.1
Total Nitrogen (mg/L)	6.4	5.8	7.4	13.5	20.2	3.2	4.3	6.2	4.9	7.5	5.2	6.9
Hardness (mg/L)	463	927	1002	330	252	191	175	258	252	276	195	1341
Phosphate (mg/L)	0.2	0.4	BL	BL	0.1	BL	BL	0.6	BL	0.1	0.5	D
TOC (mg/L)	0.7	1.3	1.5	2.1	1.8	0.5	0.5	0.7	0.6	0.5	0.5	0.9
Arsenic (mg/L)	0.06	BL	0.02	BL	0.01	0.05	0.01	0.61	0.01	BL	0.03	0.01
Calcium (mg/L)	62	128	63	25	24	9	46	12	9	29	12	88
Magnesium (mg/L)	127	137	121	107	59	52	40	54	83	51	44	137
Sodium (mg/L)	12.4	19.1	13.3	7.8	8.4	5.3	2.9	6.1	3.6	3.2	3.7	15.2
Potassium (mg/L)	6.5	3.1	3.8	4.3	2.5	1.4	1.6	1.1	2.7	2	1.8	1
Sulfate (mg/L)	32	809	896	57	49	35	13	19	13	18	5	1188
Chloride (mg/L)	139	50	72	27	41	13	12	35	16	22	17	49
Bicarbonate (mg/L)	271	194	168	271	247	203	182	231	234	248	189	104

According to the analysis conducted between June 2019 and May 2020, the average temperature values range between 14 °C and 22.5 °C in twelve monitoring wells. K8 interestingly has higher water temperatures than other locations. K8 is located close to the Tuzla Lake. We can speculate that there is an interaction between the well and surface water body, which created higher water temperatures [23].

The pH is calculated by taking the logarithm of the hydrogen ions in the solution and indicates the acidic or basic state of the solution. As a result of year-round analysis, average pH values were between 7.8 and 8.2, indicating almost neutral conditions. At all sampling points, it was between 6.5-8.5, which is pH range proposed by the WHO, for water to be used as drinking water.

The average electrical conductivity values changed between 371 and 2134 µS/cm. Electrical conductivity values increased during the summer months, most probably due to the reduction in groundwater recharge and decrease in groundwater levels, which concentrate the ions [20]. It was observed that the sampling points, K1, K2, K3, and K12, had electrical conductivity values higher than other sampling points. Electrical conductivity consists of ions dissolved in water and is an important parameter for determining water use for different purposes. In general, water quality is classified as 'good' when electrical conductivity values are between 250 and 750 µS/cm [24]. The electrical conductivity limit value determined by the WHO for drinking water is 2500 µS/cm. In this study, it was determined that all sampling wells had electrical conductivity values below the limit value set by WHO. However, in some stations the electrical conductivity values were higher than 750 μ S/cm.

Nitrate is the most common type of pollutant in groundwater systems [25]. Fertilizers used in agriculture

contain nitrate, ammonium, and organic nitrogen, and their excessive use causes nitrogen pollution due to mixing of agricultural drainage with groundwater [26]. The average value in nitrate measurements varied between 9-65 mg/L. Average values in ammonium measurements were in the range of 0.05-0.4 mg/L. While the nitrate limit value determined by the WHO for drinking water is 50 mg/L, the ammonium limit value is determined as 1.5 mg/L. Total nitrogen was in the range of 3.2 mg/L and 20.2 mg/L. Of the sampling wells, only the nitrate values measured at K4 and K5 wells exceeded the limit value of 50 mg/L. In terms of ammonium, all sample wells had ammonium concentrations below the limit value. Sampling wells with high nitrate levels were generally located at areas where agriculture and animal husbandry are common. Also the water levels in these wells are closer to the land surface, which may be increasing the risk for contamination.

The excessive use of fertilizers in agriculture causes phosphate to be adsorbed in the soil and can be mixed with groundwater after rainfall [27]. Average values in phosphate rise up to 0.6 mg/L. There is no limit value for any phosphate determined by the WHO for drinking water.

TOC originates from organic substances dissolved in water or synthetic waste from homes and industrial facilities. The average value in TOC measurements ranges from 0.5 to 2.1 mg/L. There is no TOC limit value determined by the WHO for drinking water. However, high TOC values can create a problem during chlorination as they increase the potential for trihalomethane formation [28].

The average arsenic measurements were smaller than 0.61 mg/L. The primary source of arsenic is volcanic rocks. The limit value determined by the WHO for drinking water is 0.01 mg/L. Erciyes Mountain, a volcanic mountain about 50 km away from the basin, can be associated with the amount of arsenic in the region. Similar to our study, a

previous study, conducted in the same region, identified high arsenic concentrations [29].



Fig. 6. Average values of water quality parameters

Major cations in groundwater were sodium, calcium, magnesium and potassium and major anions were chloride, bicarbonate, and sulfate (Table 2). Average concentrations of cations were in order magnesium>calcium>sodium> potassium for almost all sampling sites, while for the anions the order is as bicarbonate>chloride>sulfate for K1, K8, K9, K10, and K11 and bicarbonate>sulfate>chloride for

K4, K5, K6, and K7. K2, K3, and K12 have completely different characteristics in terms of anions. In these sites, the anion concentrations are in order as sulfate>bicarbonate>chloride. Magnesium is the dominant cation, present at concentrations range from 40 mg/L to 137 mg/L. Sulfate is the dominant anion in sampling sites, K2, K3, and K12; and bicarbonate is the dominant one in others. The concentrations of calcium and magnesium, which are multivalent (+2) cations, form hardness of water, changed between 195 and 1341 mg CaCO₃/L. Rock types such as calcite and dolomite contain calcium and magnesium [30]. The low amount of calcium and magnesium in drinking water can negatively affect bone development in children, while high concentrations can cause kidney stone formation, and arthritis problems [31, 32]. The hardness limit value determined by the WHO for drinking water is 500 mg CaCO₃/L. Sampling points other than K2, K3, and

K12, had hardness values below this limit value. According to the "French hardness" value, K1, K2, K3, K4, and K12 wells had waters in the "very hard water" class, while the others had waters in the "hard water" class.

3.3 Correlation Analysis

We conducted correlation analysis for understanding the relationships between different water quality parameters. In this analysis, we calculated Spearman correlation coefficient. The results (Table 2) showed that electrical conductivity is strongly and positively correlated with calcium (r = 0.85), magnesium (r = 0.87), sodium (r = 0.92), and sulfate (r = 0.96). This shows that aquifer chemistry is generally controlled by these ions. We also determined a strong and positive correlation between the ions sodium +, sulfate (r = 0.81), and chlorine (r = 0.61).

 Table 2. Correlation matrix of the 10 hydrogeochemical variables

Parameter	pН	EC	NO ₃	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SO4 ²	Cl	HCO ₃
pН										
EC	-0.03									
NO ₃	-0.44	0.01								
Ca ²⁺	-0.24	0.85	-0.11							
Mg ²⁺	-0.11	0.87	0.09	0.77						
Na ⁺	-0.22	0.92	0.08	0.89	0.89					
K ⁺	0.04	0.16	0.19	0.24	0.55	0.36				
SO42	-0.02	0.96	-0.09	0.79	0.74	0.81	-0.06			
Cl	0.32	0.48	-0.00	0.46	0.65	0.61	0.77	0.26		
HCO ₃	-0.11	-0.58	0.41	045	-0.22	-0.34	0.53	-0.76	0.15	

3.4 Classification of Groundwater and Suitability of Groundwater for Irrigation

The Piper diagram is commonly used in water chemistry analysis is shown in Fig. 7. The Piper diagram allows the evaluation of the hydrogeochemical types of water based on the anion and cation concentrations [33]. The diagram consists of three main regions. While the regions with equilateral triangles are composed of anions and cations, the diamond structure consists of two triangles. When the triangle with cations was examined in all sample wells, it was seen that while the triangle with the anions was "Magnesium type", the K2, K3, and K12 sample wells were "Sulfate type" waters and the remaining sample wells were in the "bicarbonate type" class. Looking at the diamond structure, it is seen that the dominant water type in the Palas Basin is "Calcium-Magnesium-Bicarbonate type" waters, while K2, K3, and K12 sampling wells are "Calcium-Magnesium-Sulfate type" waters. This can be due to the dissolution of carbonate and gypsum, calcite, and anhydrite in groundwater [34].

Sodium adsorption rate (SAR) and electrical conductivity show the probability of waters in agriculture according to the electrical conductivity and SAR ratio with the US salinity diagram [35] (Fig. 7). In Fig. 7, C1, C2, C3, C4 are located next to S1, S2, S3, S4, K1, K2, K3, K12 high saline and low sodium (C3-S1) class waters, which represent medium, high, and very salty waters. All remaining sample wells were classified as medium saline and low sodium (C2-S1) class waters. While C2-S1 class waters can be used for irrigation for salt-resistant plants, C3-S1 class waters can be used for medium and high salt-resistant plants.



Fig. 7. Piper diagram and U.S. salinity diagram

3.5 Principal component analysis (PCA)

PCA analysis was performed by including 17 parameters (pH, temperature, electrical conductivity, sodium, calcium, magnesium and potassium and major anions were chloride, bicarbonate, sulfate, nitrate, ammonium, TN, TOC, Arsenic, hardness, phosphate). The analysis was conducted using IBM SPSS Statistics Base 22.0. PCA separated the chemical variables into four orthogonal main components (PC1, PC2, PC3, PC4). The total variance of the data matrix was 85.39%. PC1 explained 37.31% of the total variance and is associated with electrical conductivity, sodium, hardness, magnesium, sulfate, and calcium. PC2, in which nitrate, TN, temperature, TOC, and pH contribute, explained 23.584% of the total variance. PC3 explains 13.96% of the variance and affected by chlorine, bicarbonate and ammonium, and finally PC4 is contributed by arsenic and phosphate, with 10.4% of the variance. The eigenvalues obtained as a result of PC1 to PC4 were 6.342, 4.009, 2.373, and 1.792, respectively. PC1 and PC3 appear to be mainly due to the dissolution of geological compounds. Contribution from human pollution sources appear in PC2 and PC4 with nitrate and phosphate (Table 3).

Table 3. Factor loadings

	Component						
Parameter	1	2	3	4			
Electrical Conductivity	0.957	0.228	-0.005	0.109			
Sodium	0.939	0.097	0.217	0.143			
Hardness	0.924	0.296	-0.106	0.084			
Magnesium	0.920	0.016	0.234	-0.123			
Sulfate	0.889	0.306	-0.243	0.152			
Calcium	0.871	0.213	0.022	0.036			
Nitrate	0.130	-0.844	0.142	0.363			
Total Nitrogen	0.127	-0.821	0.169	0.346			
Temperature	-0.231	0.776	0.361	0.314			
TOC	0.496	-0.731	0.131	0.316			
pH	-0.181	0.529	0.203	-0.480			
Chlorine	0.522	0.094	0.724	-0.340			
Potassium	0.340	-0.355	0.664	-0.522			
Bicarbonate	-0.442	-0.565	0.591	-0.147			
Ammonium	-0.413	0.335	0.413	0.039			
Arsenic	-0.350	0.410	0.433	0.568			
Phosphate	-0.232	0.428	0.537	0.546			

3.6 Hierarchical Cluster Analysis of Groundwater

Hierarchical clustering was performed using the Ward's method on 17 variable parameters obtained for 12 sample points. The analysis was conducted with Minitab 19. The difference between clusters was determined using the Euclidean distance method. The dendogram in Fig. 8 was obtained by applying the normalization process on the parameters. According to the results, 12 sample wells were divided into 3 clusters (Fig. 8).



Fig. 8. Dendrogram showing clustering of sampling wells according to groundwater quality characteristics of the Palas Basin and map showing the distribution of clusters

According to the cluster analysis result conducted according to Ward's hierarchical method, K2, K3, and K12 sampling points in the center of the Palas Basin and K1 sampling wells located in the west of the basin are located in the first cluster, while K4 and K5 sampling stations are in the second cluster group. All sampling wells are included in cluster 3, except for the K1 sampling well located to the west of the Palas Basin.

4. CONCLUSIONS

Palas Basin is a small basin located in semi-arid climatic setting. The basin is a closed basin and affected only by agriculture related impacs. The general groundwater flow in the region appears to be towards the northwest. The water level in the groundwater level measurement wells varies between 0.5 m and 47.5 m from the surface. During the summer and autumn seasons, there was a serious decrease in the water levels in the wells in the region where irrigated agriculture is carried out intensively.

It was observed that the main source of pollution affecting the groundwater quality in the study area is composed of hydrogeological processes. According to the Piper Diagram, groundwater is generally located in the Calcium-Magnesium-Bicarbonate and Calcium-Magnesium-Sulfate water facies. Sulfate levels in 3 wells (K2, K3, and K12) in the basin center exceed the limit value of 250 mg/L and are considered as "sulfate type" waters. Volcanic rocks in the region cause significant arsenic pollution in some locations. At the same time, the presence of rocks such as limestone and dolomite in the region was found to increase the calcium and magnesium concentrations in the groundwater. In terms of nitrate, except for K4 and K5 wells, the limit value of 50 mg/L was not exceeded. High phosphate values in these regions indicate that there may be a pollution caused by agriculture.

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REFERENCES

[1] V. Re, G. Zuppi, Influence of precipitation and deep saline groundwater on the hydrological systems of Mediterranean coastal plains: a general overview, *Hydrological sciences journal*, 56 (2011) 966-980.

[2] S. Kammoun, R. Trabelsi, V. Re, K. Zouari, J. Henchiri, Groundwater quality assessment in semi-arid regions using integrated approaches: the case of Grombalia aquifer (NE Tunisia), *Environmental monitoring and assessment*, 190 (2018) 87.

[3] R. Paul, K. Brindha, G. Gowrisankar, M.L. Tan, M.K. Singh, Identification of hydrogeochemical processes controlling groundwater quality in Tripura, Northeast India using evaluation indices, GIS, and multivariate statistical methods, *Environmental Earth Sciences*, 78 (2019) 470.

[4] R. Avtar, P. Kumar, A. Surjan, L. Gupta, K. Roychowdhury, Geochemical processes regulating

groundwater chemistry with special reference to nitrate and fluoride enrichment in Chhatarpur area, Madhya Pradesh, India, *Environmental earth sciences*, 70 (2013) 1699-1708. [5] S. Siebert, J.J. Burke, J.M. Faurès, K. Frenken, J. Hoogeveen, P. Döll, F.T. Portmann, Groundwater use for irrigation - a global inventory, *Hydrology and Earth System Sciences*, 14 (2010) 1863-1880.

[6] S. Dangar, A. Asoka, V. Mishra, Causes and implications of groundwater depletion in India: A review, *Journal of Hydrology*, 596 (2021) 126103.

[7] H. Jia, H. Qian, L. Zheng, W. Feng, H. Wang, Y. Gao, Alterations to groundwater chemistry due to modern water transfer for irrigation over decades, *Science of The Total Environment*, 717 (2020) 137170.

[8] A. Pulido-Bosch, J.P. Rigol-Sanchez, A. Vallejos, J.M. Andreu, J.C. Ceron, L. Molina-Sanchez, F. Sola, Impacts of agricultural irrigation on groundwater salinity, *Environmental Earth Sciences*, 77 (2018) 197.

[9] M. Cetin, Agricultural Water Use, in: N.B. Harmancioglu, D. Altinbilek (Eds.) *Water Resources of Turkey*, Springer International Publishing, Cham, 2020, pp. 257-302.

[10] DSİ, *Turkey Water Report 2009*, in, Devlet Su İşleri, Ankara, 2009.

[11] S. Ekercin, E. Sertel, F. Dadaser-Celik, S. Durduran, Investigating the Climate Change Impacts on the Water Resources of the Konya Closed Basin Area (Turkey) Using Satellite Remote Sensing Data, in: İ. Dincer, C.O. Colpan, F. Kadioglu (Eds.) *Causes, Impacts and Solutions to Global Warming*, Springer Science+Business Media, New York, 2013.

[12] F. Dadaser-Celik, M. Celik, Modelling surface watergroundwater interactions at the Palas Basin (Turkey) using FREEWAT, *Acque Sotterranee - Italian Journal of Groundwater*, 6 (2017) 53-60.

[13] S.T. Azgin, F. Dadaser-Celik, Spatial and temporal changes at Tuzla (Palas) Lake in Turkey, *Journal of Water and Climate Change*, 6 (2015) 787-799.

[14] S.T. Azgin, F. Dadaser-Celik, Evaluating Surface Runoff Responses to Land Use Changes in a Data Scarce Basin: a Case Study in Palas Basin, Turkey, *Water Resources*, 47 (2020) 828-834.

[15] G. De Filippis, C. Pouliaris, D. Kahuda, T.A. Vasile, V.A. Manea, F. Zaun, B. Panteleit, F. Dadaser-Celik, P. Positano, M.S. Nannucci, M. Grodzynskyi, A. Marandi, M. Sapiano, I. Kopač, A. Kallioras, M. Cannata, Y. Filiali-Meknassi, L. Foglia, I. Borsi, R. Rossetto, Spatial Data Management and Numerical Modelling: Demonstrating the Application of the QGIS-Integrated FREEWAT Platform at 13 Case Studies for Tackling Groundwater Resource Management, *Water*, 12 (2020).

[16] B. Helena, R. Pardo, M. Vega, E. Barrado, J.M. Fernandez, L. Fernandez, Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga River, Spain) by principal component analysis, *Water Research*, 34 (2000) 807-816.

[17] M. Vega, R. Pardo, E. Barrado, L. Debán, Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis, *Water Research*, 32 (1998) 3581-3592.

[18] T. Subramani, N. Rajmohan, L. Elango, Groundwater geochemistry and identification of hydrogeochemical processes in a hard rock region, Southern India, *Environmental monitoring and assessment*, 162 (2010) 123-137.

[19] R. Chatterjee, G. Tarafder, S. Paul, Groundwater quality assessment of Dhanbad district, Jharkhand, India, *Bulletin of engineering geology and the environment*, 69 (2010) 137-141.

[20] L. Kiewiet, J. von Freyberg, H.J. van Meerveld, Spatiotemporal variability in hydrochemistry of shallow groundwater in a small pre-alpine catchment: The importance of landscape elements, *Hydrological Processes*, 33 (2019) 2502-2522.

[21] S. He, J. Wu, Hydrogeochemical characteristics, groundwater quality, and health risks from hexavalent chromium and nitrate in groundwater of Huanhe Formation in Wuqi county, northwest China, *Exposure and Health*, 11 (2019) 125-137.

[22] M. Tomlinson, A.J. Boulton, Ecology and management of subsurface groundwater dependent ecosystems in Australia–a review, *Marine and Freshwater Research*, 61 (2010) 936-949.

[23] J. Ren, J. Cheng, J. Yang, Y. Zhou, A review on using heat as a tool for studying groundwater–surface water interactions, *Environmental Earth Sciences*, 77 (2018) 756.
[24] K. Prakash, R. Somashekar, Groundwater quality-Assessment on Anekal Taluk, Bangalore Urban district, India, *Journal of Environmental Biology*, 27 (2006) 633-637.

[25] V. Goldberg, Groundwater pollution by nitrates from livestock wastes, *Environmental Health Perspectives*, 83 (1989) 25-29.

[26] I. Marinov, A.M. Marinov, A coupled mathematical model to predict the influence of nitrogen fertilization on crop, soil and groundwater quality, *Water resources management*, 28 (2014) 5231-5246.

[27] O.K. Borggaard, C. Szilas, A.L. Gimsing, L.H. Rasmussen, Estimation of soil phosphate adsorption capacity by means of a pedotransfer function, *Geoderma*, 118 (2004) 55-61.

[28] N. Ates, S.S. Kaplan-Bekaroglu, F. Dadaser-Celik, Spatial/temporal distribution and multi-pathway cancer risk assessment of trihalomethanes in low TOC and high bromide groundwater, *Environmental Science: Processes* & Impacts, 22 (2020) 2276-2290.

[29] C. Simsek, Assessment of naturally occurring arsenic contamination in the groundwater of Sarkisla Plain (Sivas/Turkey), *Environmental Earth Sciences*, 68 (2013) 691-702.

[30] S. Sargazi, M. Mokhtari, M.H. Ehrampoush, S.A. Almodaresi, H. Sargazi, M. Sarhadi, The application of geographical information system (GIS) approach for assessment of groundwater quality of Zahedan city, Sistan and Baluchestan Province, Iran, *Groundwater for Sustainable Development*, (2020) 100509.

[31] Y. Huang, X. Ma, Y. Tan, L. Wang, J. Wang, L. Lan, Z. Qiu, J. Luo, H. Zeng, W. Shu, Consumption of very low Mineral water is associated with lower bone mineral content in children, *The Journal of nutrition*, 149 (2019) 1994-2000.

[32] F. Kozisek, Regulations for calcium, magnesium or hardness in drinking water in the European Union member states, *Regulatory Toxicology and Pharmacology*, 112 (2020) 104589.

[33] A.M. Piper, A graphic procedure in the geochemical interpretation of water-analyses, *Eos, Transactions American Geophysical Union*, 25 (1944) 914-928.

[34] F. Ehya, Z. Marbouti, Hydrochemistry and contamination of groundwater resources in the Behbahan plain, SW Iran, *Environmental Earth Sciences*, 75 (2016) 455.

[35] L.A. Richards, *Diagnosis and improvement of saline and alkali soils*, LWW, 1954.