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INVESTIGATION OF THE WATER RESOURCES IN KÖPRÜÖREN BASIN (KÜTAHYA) WITH ENVIRONMENTAL ISOTOPES

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Research Article

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ABSTRACT

In this study, the isotopic properties of the water resources located in Köprüören Basin are determined. $\delta^{18}O$ and δD contents of the samples respectively ranged from -10.84‰ to -7.09‰ and from -73.6‰ to -53.3‰ in dry season and ranged from -10.81‰ to -4.71‰ and -73.3‰ to -41.5‰ in wet season. Majority of the samples plotted along Global Meteoric Water Line although some of them show deviations from this line. The reason for the deviations are attributed to evaporative enrichment, modifying the original $\delta^{18}O$ and δD signatures of the samples. $\delta^{18}O$ content of the thermal samples are not modified as a result of water-rock interaction due to low wellhead and reservoir temperatures. Tritium concentrations for all samples range from ~0 to 6 TU in wet season and from ~0 to 8 TU in dry season. Accordingly, some of the groundwater samples are recharged from modern precipitation, their groundwater residence times are short and they have shallow circulation. Besides, samples with tritium concentrations close to detection limits (thermal water samples and two of the groundwater samples) were recharged before tritium from nuclear weapon tests and have relatively higher residence times. These samples were also analysed for $\delta^{13}C$ and ^{14}C to get information about the residence times. $\delta^{13}C$ ve percent modern carbon contents of five samples range from -5‰ to -14.6‰ and from 8.2 to 78 pmc, respectively. The corrected ^{14}C ages for these samples are up to 11500 years before present, thereby indicating the presence of paleowaters in the basin. $\delta^{13}C$ data indicate that ^{14}C contents of the thermal waters were diluted as a result of water-rock interaction.

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1. Introduction

The importance of sustainable management of water resources has been increasing in recent years due to the rise in water consumption triggered with various factors including global population increase, industrial revolution and climate change. At the present time Turkey is not considered as one of the water-stressed countries, however, the pressure in our water resources increase with urbanization, industrialization, population and irrigation water requirement. Therefore, it is necessary to use advanced techniques, besides the classic methods to contribute to the research carried out towards safe and sustainable development of the available water resources which are renewable but limited (Çifter and Sayın, 2002). Isotope techniques have commonly been employed in hydrological and hydrogeological investigations. Humans cannot control the signature of environmental isotopes found naturally in water, therefore, in hydrology monitoring and evaluation of isotopic variations give information about the origin and renewability of waters, recharge areas and circulation mechanisms, mixing processes, surface water- groundwater interactions, and the subsurface processes affecting the quality of waters (Clark and Fritz, 1997). Many researchers have employed environmental isotopes in investigations involving determination of groundwater flow paths, groundwater residence times and water circulation (Schlosser et al., 1988; Clark et al., 1997; Bayarı et al., 2009; Çelik et al., 2013; Arslan et al., 2015).

Köprüören Basin is located to the west of the Kütahya province, upstream of Kütahya and Eskişehir plains (Figure 1). The total catchment area of the basin is 320 km^2; however, both the quality and the quantity of the basin influences a broader region than the catchment area itself involving Enne Dam, Felent and Porsuk streams. The only exploited silver deposit of Turkey is developed in the metamorphic basement rocks, Early Miocene volcanics and Pliocene units. The cyanide-rich wastes of the silver plant are stored in waste pools. The safety of this facility has been discussed and investigations have been carried out to put forward

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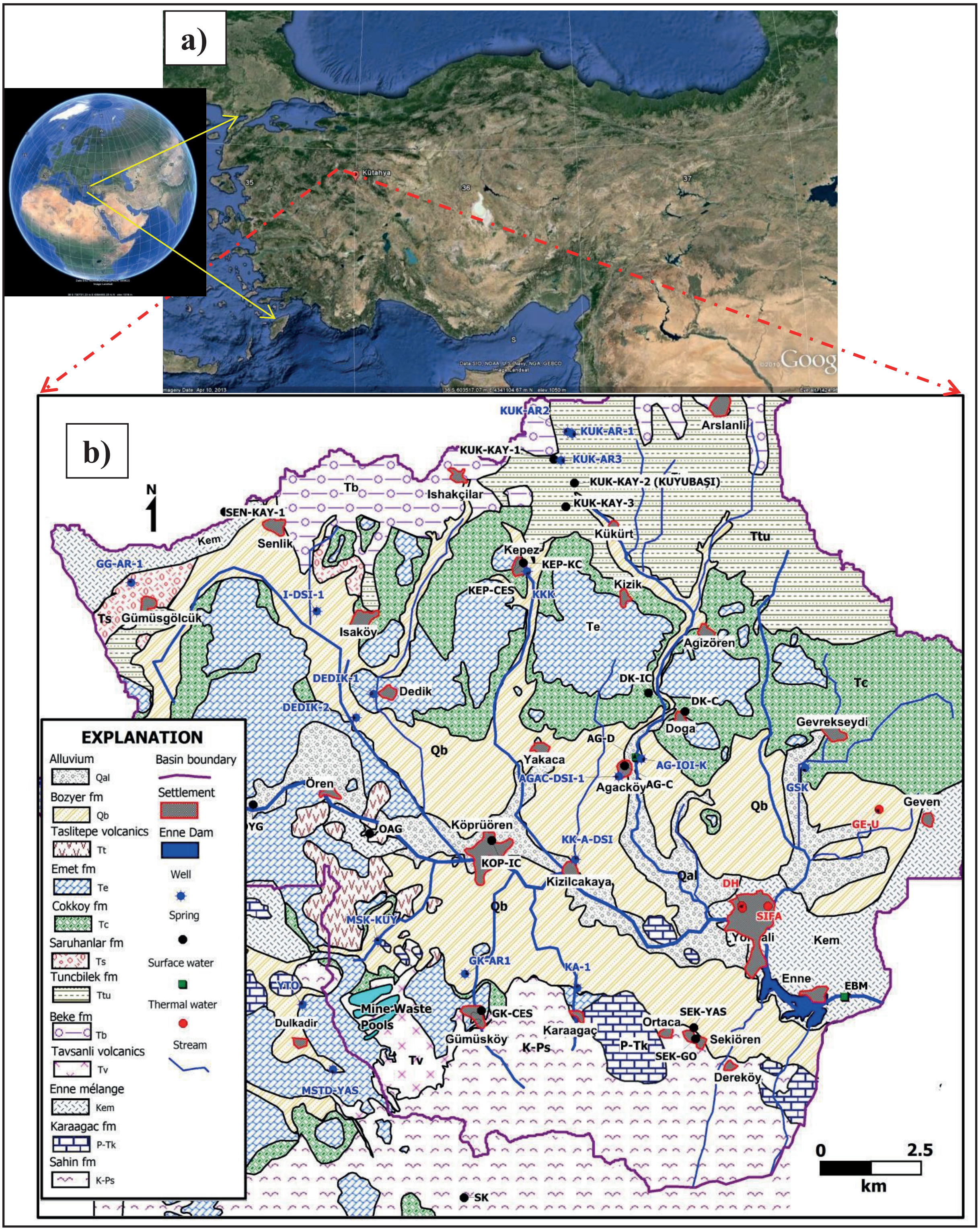

Figure 1- Figure showing a) location map b) geological map of the study area with sampling locations (Modified from Arik, 2002).

the damage to the environment after a major collapse occurred in one of the pools (Arslan et al., 2013; Arslan and Çelik, 2015)

The aim of this study is to present the isotopic signatures and origin of the water resources in Köprüören Basin as well as to determine the groundwater residence times and to identify different processes (evaporation, water-rock interaction etc.) involved in the modification of the isotopic composition of the waters. To this end, the stable isotopes of oxygen, hydrogen and carbon ($\delta^{18}O$, δD and $\delta^{13}C$) and the radioactive isotopes of hydrogen and carbon (^{3}H and ^{14}C) are utilized.

1.1. Geographical Setting, Climate and Topography

Köprüören Basin is located in Inner West Anatolia, to the north of Kütahya province and to the south of Tavşanlı district. The effects of both continental and Mediterranean climates can be seen in the area. Summers are generally hot and dry whereas winters are moist and cold. The annual average mean temperature, precipitation, average relative humidity and potential evapotranspiration recorded at Kütahya Meteorological Station between years 1970-2913 by Turkish State Meteorological Service are 10.7 °C, 546.5 mm, 65% and 800 mm, respectively. The elevation within the basin varies between 900 m and 1600 m and the average elevation is 1250 m. Northern and southern parts have rugged terrains, whereas the central part is flat (Figure 2).

1.2. Geological and Hydrogeological Settings

The geologic units outcropping in the study area are represented by metamorphic, magmatic, volcanic and sedimentary rocks formed between Paleozoic and Quaternary periods (Figure 1) Arık, 2002). Basement rocks in the area are Palezoic (Carboniferous- Permian) metamorphics which are composed of metasandstones, metaconglomerates and schists (Baş, 1983; 1986; 1987; Arık, 2002). Paleozoic metamorphics are also known as Şahin formation. Şahin formation is conformably overlain by Karaağaç Formation consisting of Permian-Triassic marbles (Arık, 2002). These marbles are

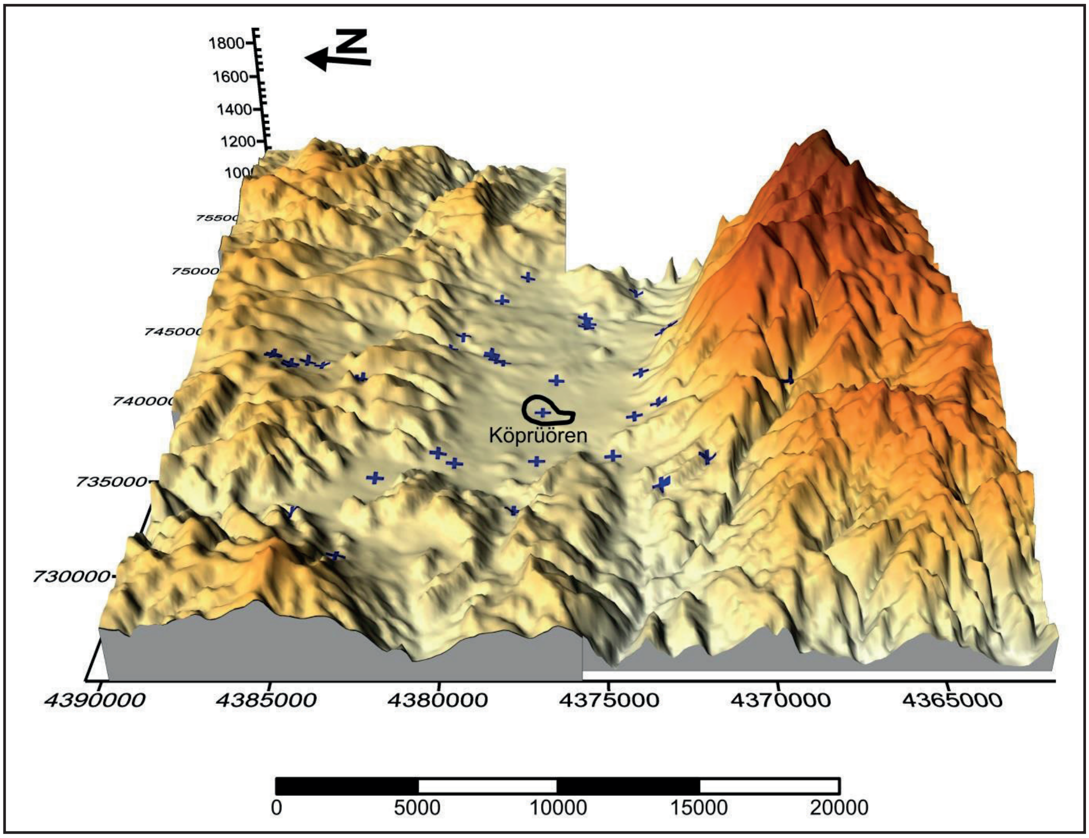

Figure 2- Digital elevation model of the study area. Sampling locations are shown with blue plus signs.

dark grey colored, thick layered at the bottom and thin to medium layered at the top. The older units are tectonically overlain by Upper Cretaceous Enne mélange consisting of serpentinite, cherts and radiolarites (Arık, 2002). Due to the block faulting in Late Oligocene- Early Miocene two different depositional settings were formed in the area. In the northern part, pre-Cenozoic units are unconformably overlain by Early Miocene Beke formation. Beke formation contains pebble stone, sandstone, mudstone, shale, bituminous levels rich in organic matter and coal lenses (lignites) (Konak, 1979; Baş, 1983; Çelik ve Kerey, 1999; Arık, 2002). The pebbles of this formation are derived from schists, carbonate rocks and serpentinites. Beke formation is conformably overlain by Miocene Tunçbilek formation which is composed of claystone-siltstone alternations, laminated tuffite and calcareous claystone at the base; coal lenses represented by dark brown, black colored lignites (Çelik and Kerey, 1999) in the middle followed by laminated marls, clayey limestones, claystones and silicified tuffs at the top. In the southern part of the study area, pre-Cenozoic units are unconformably overlain by Tavsanli volcanics which consist of altered dacites, rhyodacites, tuffs and agglomerates. The oldest unit of Pliocene, Saruhanlar formation can be observed throughout the basin and it covers the older units unconformably. This formation is composed of conglomerates, sandstones and alternations of limestone and tuffs (Baş, 1983). Late Pliocene Çokköy formation overlies Saruhanlar formation conformably and consists of marls, claystones, sandstones, conglomerates and tuff. Çokköy formation is conformably overlain by Early Pliocene Emet formation. Emet formation is composed of highly porous, white limestones, clayey, silicified and dolomitic limestones (Akdeniz and Konak, 1979). At the bottom of this formation, clayey limestones and marls are abundant. Limestones of Emet formation show thin laminations and in between them there are clayey and cherty levels. Furthermore, Arik (2002) stated that there are cavities formed due to dissolution. There is volcanic input in early Pliocene during which Taşlıtepe volcanics formed. Taşlıtepe volcanics are characterized by black, highly porous basalts and dark pink colored andesites (Baş, 1983). Quaternary Bozyer formation and alluvium deposits unconformably overlie the older units. Bozyer formation shows a wide distribution in the basin and contains red pebbles, sands and clays. Today, weathering still continues contributing to the formation of alluvium (Arık, 2002).

Kocasu stream and its tributaries are the surface waters of the basin with a drainage area of 320 km^2 (Figure 1). Kocasu stream flows from west to east into Enne Dam in Yoncalı. This stream joins to Felent Stream, flows to east until it reaches Porsuk River. Enne Dam is the main reservoir in the basin and is used for irrigation and for cooling purposes in Seyitömer thermal plant located to the north of the basin.

State Hydraulic Works (DSİ) carried out hydrogeological investigations in 1981 and determined the locations of the alluvium springs which were formed along the contact of the water table and topography and the karstic springs. Moreover, there are some thermal springs located around Yoncalı village. These springs emerge along the faults in Paleozoic marbles. The main aquifer units in the area were determined by the geological and geophysical investigations and exploration drilling carried out by DSİ (DSİ, 1981). Accordingly, Quaternary units are clayey and they are not considered as a productive aquifer. Limestones and tuffs in Neogene series, on the other hand, are the water bearing units in the area and the main aquifer. The groundwater flow in the plain part of the basin is from north to south and south to north towards Kocasu stream and there is discharge to Enne Dam. There are 6 irrigation cooperatives throughout the basin (Dedik, Yakaca, Ağaçköy, Kızılcakaya, Köprüören, Gümüşköy) which were established to employ groundwater for irrigation purposes. Only the ones located in Dedik, Gümüşköy, Kızılcakaya and Ağaçköy are active. In other parts of the basin, there are a limited number of wells used for irrigation.

According to the hydrogeochemical studies conducted by Arslan and Çelik (2013) the dominant cations in the waters of the basin are Ca and Mg, whereas the dominant anions are HCO_3 and SO_4 (Table 1). The chemical characters of the samples are in general Ca-Mg-HCO_3 and Mg-Ca-HCO_3 except for one well located in Gümüşgölcük village which is Na-HCO_3 type (Arslan and Çelik, 2013).

Table 1- The coordinate and altitude information, sample explanations, water types and the in-situ electrical conductivities of the samples determined in May 2012 and September 2012.

Sample ID	X	Y	Altitude (m)	EC (µS/cm)		Chemical Character (Arslan and Çelik, 2013)	Explanation
				May 2012	September 2012		
OAG	734678	4377301	1024	573	518	Mg-Ca-HCO$_3$	Spring emerging from volcanics (sample taken from discharge point inside a lake)
KK-A-DSI	739718	4376655	1035	518	774	Mg-Ca-HCO$_3$	Kızılcakaya village DSİ irrigation well No: 41052
GG-AR-1	728846	4383426	1108	402	389	Na-HCO$_3$	Gümüşgölcük village well (artesian)
SK	736997	4368394	1233	484	507	Ca-Mg-HCO$_3$	Fountain located in the entrance of Şahin village
I-DSI-1	733384	4382727	1055		881	Mg-Ca-HCO$_3$	İsaköy village DSİ irrigation well No: 55505
EBM	746560	4373445	998	485		Mg-Ca-HCO$_3$	Surface water sample located downstream of Enne Dam
YTO	733039	4373105	1080			Ca-Mg-HCO$_3$	Well located in Yılmazlar stone quarry
KUK-KAY-1	739192	4386460	1150			Mg-Ca-HCO$_3$	Kükürt village spring
KUK-KAY-2 (KUYUBAŞI)	739699	4385874	1125	1600	1572	Mg-Ca-SO$_4$-HCO$_3$	Kükürt village spring
KUK-KAY-3	739489	4385299	1128		1101	Mg-Ca-HCO$_3$	Kükürt village spring
GSK	745350	4378900	1034	820		Mg-Ca-HCO$_3$	Gevrekseydi village DSİ irrigation well No: 55227
KUK-AR-1	739641	4387068	1171	760		Mg-Ca-HCO$_3$	Kükürt village artesian well
SIFA	744435	4375525	1000			Ca-Mg-HCO$_3$	Şifa hotel well- Mixture of thermal water and groundwater
YKK	743794	4375531	1007		990	Ca-Mg-HCO$_3$	Yoncalı Thermal Hotel well- thermal water
DH	743807	4375477	1006			Ca-Mg-HCO$_3$	Dübecik Hamam well- thermal water
SEN-KAY-1	731131	4385175	1077			Mg-HCO$_3$	Şenlik village spring
KKK	738535	4383710	1135			Mg-Ca-HCO$_3$	Kepez village well
AG-C	740923	4378959	1047	356		Mg-Ca-HCO$_3$	Ağaçköy fountain
AG-IOI-K	741337	4379120	1038	1194		Mg-Ca-HCO$_3$-SO$_4$	Ağaçköy Special provincial Administration well
AG-D	741210	4379158	1035	1600		Mg-Ca-SO$_4$-HCO$_3$	Ağaçköy stream
DK-C	742403	4380288	1058	1345	1122	Mg-Ca-HCO$_3$-SO$_4$	Doğaköy fountain
DK-IC	741511	4380739	1054	378	352	Mg-Ca-HCO$_3$	Doğaköy drinking water fountain
OYG	731833	4378007	1032	613	956	Mg-Ca-HCO$_3$	Spring located west of Ören village
SEK-YAS	742618	4372554	1071	671	1010	Ca-Mg-HCO$_3$	Sekiören village fountain
SEK-GO	742666	4372278	1100	551	381	Mg-Ca-HCO$_3$	Sekiören village spring located prior to a pond
KOP-IC	737670	4377130	1018	569		Mg-Ca-HCO$_3$	Köprüören village drinking water fountain
KEP-CES	738444	4383924	1153	573	600	Mg-Ca-HCO$_3$	Kepez village fountain
KUK-AR2	739530	4387123	1173	870		Mg-Ca-HCO$_3$	Kükürt village artesian well
KUK-AR3	739367	4386420	1146	958		Mg-HCO3	Kükürt village artesian well
GK-AR1	737018	4373857	1049	590	704	Ca-MgHCO$_3$	Gümüşköy DSİ irrigation well No: 52884
GE-U	747156	4377891	1038	533	1102	Mg-Ca-HCO$_3$	Thermal water well located in Geven village (Belongs to Dumlupınar University)
Y-YAG	744060	4375408	990			Ca-HCO$_3$-SO$_4$	Rain sampled in Yoncalı village
MSK-KUY	734890	4374659	1031	410		Ca-Mg-Na-HCO$_3$	Well located downstream of mine site
MSTD-YAS	733788	4371522	1113	426		Ca-HCO$_3$	Well close to Dulkadir village
AGAC-DSI-1	740779	4378690	1043		823	Mg-Ca-HCO$_3$	Ağaçköy DSİ irrigation well No: 36813
GK-CES	737419	4372971	1094		636	Ca-HCO$_3$	Gümüşköy fountain
KA-1	739768	4373513	1068		736	Ca-Mg HCO$_3$	Karaağaç village well
DEDIK-1	734779	4380705			660	Mg-Ca-HCO$_3$	Dedik village DSİ irrigation well No: 41946
DEDIK-2	734350	4380125	1042		665	Mg-Ca-HCO$_3$	Dedik village DSİ irrigation well No: 41949
KEP-KC	738444	4383924	1137		600	Mg-Ca-HCO$_3$	Kepez village fountain

2. Sampling and Analysis Procedures

Three field trips were carried out between years 2011 and 2012 and in-situ electrical conductivity (EC) measurements were performed in surface waters, groundwaters, springs and thermal springs in 40 different locations. Deuterium (δD) and oxygen-18 (δ^{18}O) samples were collected from each of these locations. Besides, 20 samples were collected for tritium analyses (^{3}H) and 5 samples were collected for carbon-13 (δ^{13}C) and carbon-14 (^{14}C) analyses. For radiocarbon samples, in order to prevent post-collection biological activity from altering the carbon concentration and isotopic concentration, the samples were preserved by adding approximately 0.2 ml of saturated $HgCl_2$ solution.

Samples collected in October 2011 and September 2012 represent dry periods whereas the samples collected in May 2012 represent wet period. For **δ^{18}**O and δD analyses, 17, 25 and 22 samples were collected in October 2011, May 2012 and September 2012, respectively. In selected locations, to observe the seasonal changes, samples were taken in all of the three sampling periods. For ^{3}H analyses, 5, 12 and 14 samples were collected in October 2011, May 2012 and September 2012, respectively (Table 2). Sampling was carried out only in September 2012 for δ^{13}C and ^{14}C (Table 3).

The water samples were analyzed for their δ^{18}O and δD stable isotope ratios in the Stable Isotope Laboratory of Hacettepe University by using laser spectroscopic methods. VSMOW (Vienna Standard Mean Ocean Water) was used as a reference standard and analytical precisions were reported to be within 0.2‰ for δ^{18}O and 1‰ for δD. ^{3}H concentrations were determined in the Environmental Tritium Laboratory of Hacettepe University with an ultra-low level liquid scintillation counting unit. Analytical uncertainties are reported as ±0.4 TU. δ^{13}C and ^{14}C analyses were carried out in Beta Analytical Laboratories (U.S.A.) from dissolved inorganic carbon (DIC). δ^{13}C contents were determined by using a Stable Isotope Mass Spectrometer whereas carbon-14 analyses were carried out by using an accelerator mass spectrometry (AMS) system

3. Results and Discussion

3.1. Relationship of Oxygen-18 (δ^{18}O) and Deuterium (δD)

According to the electrical conductivity measurements carried out during the field trips in May 2012 and September 2012, EC values vary between 356 µS/cm and 1600 µS/cm for 24 samples in May 2012 and they vary between 352 µS/cm and 1572 µS/cm for 22 samples (Table 1).

Results of the environmental isotopic analyses are reported in Table 2 for October 2011, May 2012 and September 2012. Accordingly, not much seasonal difference can be observed in samples collected from the same location in different periods (dry and wet periods) except for samples EBM, SEK-GO, KEP-CES and GE-U. For samples collected in dry period, δ^{18}O and δD values range from -10.84‰ to -7.09‰ and from -73.6‰ to -53.3‰, respectively (Table 2). Deuterium excess values, calculated by using formula d= δD-8* δ^{18}O, are also presented in Table 2 and they vary between 3.5 ‰ and 13.9 ‰ in October 2011, between -3.8 ‰ and 13.2 ‰ in May 2012 and between 5.22 ‰ and 14.94 ‰ in September 2012.

To understand the relationship between δ^{18}O and δD, δ^{18}O vs. δD graphs were prepared for each sampling season and data were compared to Global and Mediterranean Meteoric Water Lines (GMWL and MMWL) (Figure 3, 4, 5). According to figure 3, some of the samples collected in October 2011 plotted along GMWL whereas some of them show deviations from the GMWL. Deviations from meteoric water lines are usually caused by different processes like evaporation, condensation, water-rock interaction. During evaporation, lighter isotopes enter the vapor phase immediately, therefore, the remaining water phase enriches in heavy isotopes (Clark and Fritz, 1997). An evaporation line with a slope of approximately 5 was formed with the samples showing deviation from GMWL. The slope of this line (s) depends on the relative humidity since oxygen and hydrogen are affected by moisture differently and if the relative humidity is between 25% and 75% the slope is usually between 4 and 5 (Clark and Fritz, 1997). The average relative humidity in the area is reported as 65% by Turkish Meteorological Service and the slope of the evaporation line is coherent with the relative humidity. In figure 3 one sample, which shows maximum

Table 2- Oxygen-18, deuterium, deuterium excess and tritium data for October 2011, May 2012 and September 2012.

Sample ID	Deuterium (‰)			Oxygen-18 (‰)			Döteryum fazlalığı (‰)			Trityum (TU)		
	October 2011	May 2012	September 2012	October 2011	May 2012	September 2012	October 2011	May 2012	September 2012	October 2011	May 2012	September 2012
OAG	-60.3	-61.8	-61.2	-8.57	-8.56	-8.55	8.3	6.7	7.2		3.44	
KK-A-DSI	-62.5	-63.3	-65.3	-8.71	-8.8	-9.01	7.2	7.1	6.7		0.6	-0.4
GG-AR-1	-71.5	-72.1	-72.8	-10	-9.98	-10.19	8.5	7.8	8.7		-0.41	0.87
SK	-68.3	-73.3	-73.6	-10.29	-10.81	-10.62	14.0	13.2	11.4	4.11	5.41	
I-DSI-1	-65.1		-66.4	-9.05		-9.24	7.3		7.6			5.66
EBM	-53.3	-68.2		-7.09	-9.67		3.5	9.2				
YTO	-63.3			-8.88			7.7					
KUK-KAY-1	-61.1			-8.59			7.6			7.87		
KUK-KAY-2 (KUYUBAŞI)	-62.2	-61.3	-63.9	-8.6	-8.48	-8.82	6.6	6.5	6.7			6.3
KUK-KAY-3	-60.1		-63.5	-8.4		-8.59	7.1		5.2			
GSK	-63.4	-64.7		-8.68	-8.95		6.0	6.9		2.44	0.79	1.69
KUK-AR-1	-60.6	-61.1		-8.63	-8.55		8.4	7.3		2.55	4.58	6.57
SIFA	-65.3			-9.23			8.5					
YKK	-68.3		-70.0	-9.86		-9.88	10.6		9.1	0.3		
DH	-66.8			-9.78			11.5					
SEN-KAY-1	-63.2			-9.03			9.0					2.95
KKK	-61.2			-8.76			8.9					
AG-C		-64.5			-9.11			8.4				
AG-IOI-K		-60.8			-8.28			5.5				
AG-D		-58.4			-8.05			6.0				
DK-C		-62.6	-63.0		-8.78	-9.11		7.6	9.9		1.18	
DK-IC		-65.3	-63.6		-9.11	-9.03		7.6	8.6			
OYG		-61.4	-62.0		-8.5	-8.7		6.6	7.6		6.11	6.44
SEK-YAS		-71.6	-68.4		-10.55	-10.08		12.8	12.2		5.33	6.74
SEK-GO		-71.6	-69.9		-10.47	-10.61		12.1	14.9			
KOP-IC		-60.6			-8.3			5.8				
KEP-CES		-61.9	-65.0		-8.87	-9.19		9.1	8.6			7.23
KUK-AR2		-62.2			-8.84			8.5			3.48	
KUK-AR3		-62.4			-8.78			7.9				
GK-AR1		-67.3	-69.1		-9.72	-10.23		10.4	12.7		5.06	3.61
GE-U		-64.7	-73.4		-8.73	-10.53		5.2	10.9		1.02	0.48
Y-YAG		-34.5			-5.79			11.8				
MSK-KUY		-41.5			-4.71			-3.8				
MSTD-YAS		-63.3			-9.33			11.4				
AGAC-DSI-1			-63.8			-8.71			5.9			1.33
GK-CES			-72.6			-10.84			14.2			
KA-1			-66.9			-9.81			11.6			
DEDIK-1			-63.3			-8.95			8.3			4.31
DEDIK-2			-62.7			-8.58			6.0			
KEP-KC			-65.9			-9.07			6.7			

Table 3- $\delta^{13}C$ and ^{14}C data, radiocarbon ages without correction, q-factor, apparent radiocarbon ages corrected with carbon-13 method.

Sample ID	$\delta^{13}C$ (‰)	^{14}C (pmc)	^{14}C Error (pmc)	Unadjusted ^{14}C age (BP*)	^{14}C age error (BP)	q factor	Corrected ^{14}C ages (BP)
GE-U	-5.0	8.18	0.09	20110	90	0.26	9420
KK-A-DSI	-11.4	19.10	0.12	13300	50	0.48	7375
GG-AR-1	-14.6	13.99	0.1	15800	60	0.59	11500
GSK	-13.3	77.96	0.28	2000	30	0.54	-2920
YKK	-4.8	13.18	0.09	16280	60	0.26	5380

* Radiocarbon ages were calculated by assuming an initial ^{14}C content of 100 pmc for the water samples. Libby half-life ($t_{1/2}$ =5568 years) was used in the calculations.

evaporative enrichment, was collected from Enne Dam and this sample was exposed to evaporation under high temperature conditions during the dry period. For other samples located along the evaporation line there is also evaporative enrichment. Some of the fountain samples were not collected from their original sources where they emerge, so evaporative enrichment is possible during storage. For shallow wells, evaporation before recharge can be the reason of the evaporative enrichment of these samples.

Thermal water samples do not show evaporative enrichment and they have depleted $\delta^{18}O$ and $\delta^{2}H$ values. Besides, these samples are plotted along GMWL although deviations in $\delta^{18}O$ due to the water-rock interaction are common in thermal waters. The thermal waters, under high temperatures, usually interact with rocks and during this interaction there is enrichment in $\delta^{18}O$ values of the waters (the hydrogen contents of the rocks are usually lower compared to the hydrogen contents of water so during water-rock interaction δD contents doesn't show variations.) (Güleç and Mutlu, 2002). The wellhead temperatures of thermal waters sampled in Yoncali are around 40 °C (Arslan and Çelik, 2013). Besides, the reservoir temperatures calculated by using chalcedony and quartz geothermometers (Fournier, 1977) ranges between 49-84 °C for Yoncalı, and between 68-99 °C for Geven (Arslan and Çelik, 2013). Therefore, due to the reason that thermal waters have relatively low wellhead and reservoir temperatures, the $\delta^{18}O$ contents of these samples are not affected from the water-rock interaction. One of the samples collected from Yoncali has got $\delta^{2}H$ and $d^{18}O$ content similar to the $\delta^{2}H$ and $d^{18}O$ of cold waters (Figure 3). This sample was collected from a pool in which a mixture of thermal and cold waters was present. Therefore, this sample reflects the isotopic content of a mixture instead of reflecting the isotopic contents of a thermal water sample. There are two samples having relatively depleted stable isotope contents compared to the thermal waters (Figure 3). One of these samples was collected from an artesian well located in Gümüşgölcük village and it will be evaluated in the following sections. The other sample was collected from a fountain in the entrance of Şahin village (SK, discharge elevation: 1233 m). The tritium content of SK is 4.11 TU and due to the presence of tritium, it can be argued that this sample is recharged with modern precipitation falling into high altitudes.

According to figure 4, which was prepared by using stable isotope data obtained during wet period sampling, there is an evaporation line formed with a slope of 5 in accordance with the relative humidity. This evaporation line is similar to the one presented in figure 3. Herein, the sample showing maximum evaporation effect is collected from a well sample located downstream of the silver mine site. In this well it was not possible to discharge the water prior to sampling so the sample was taken from the evaporated water mass inside the well. Another sampling point which is on the evaporation line is stream water sampled near Ağaçköy and observation of evaporation effect in surface water is an expected result. Another noteworthy point about evaporation is that in Enne Dam samples, the dry period sample is under the influence of evaporation although the sample collected in wet period does not show evaporation effects according to $\delta^{2}H$- $\delta^{18}O$ contents. In the sample location, the difference in dam water level between dry and wet periods and the change in isotope content with the effect of rain is stunning. In this period, rain water sampling was possible following heavy rains in Yoncalı region. $\delta^{2}H$- $\delta^{18}O$ content of this sample almost plotted along Global Meteoric Water Line (Figure 4). In May 2012, thermal water sampling was carried out in one station which belongs to Dumlupınar University located

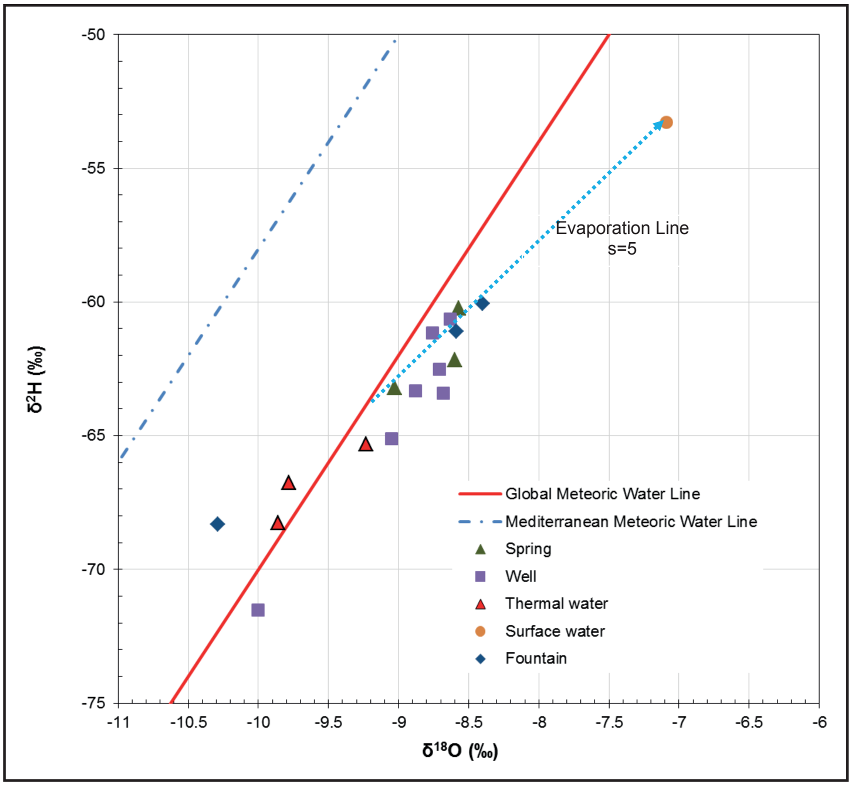

Figure 3- δ^2H vs. $\delta^{18}O$ diagram for October 2011 (dry period). Global Meteoric Water Line is defined by equation $\delta^2H = 8\delta^{18}O+10$ (‰ SMOW) (Craig, 1961), Mediterranean Meteoric Water Line is defined by equation $\delta^2H = 8\delta^{18}O+22$ (‰ SMOW) (Gat and Carmi, 1970).

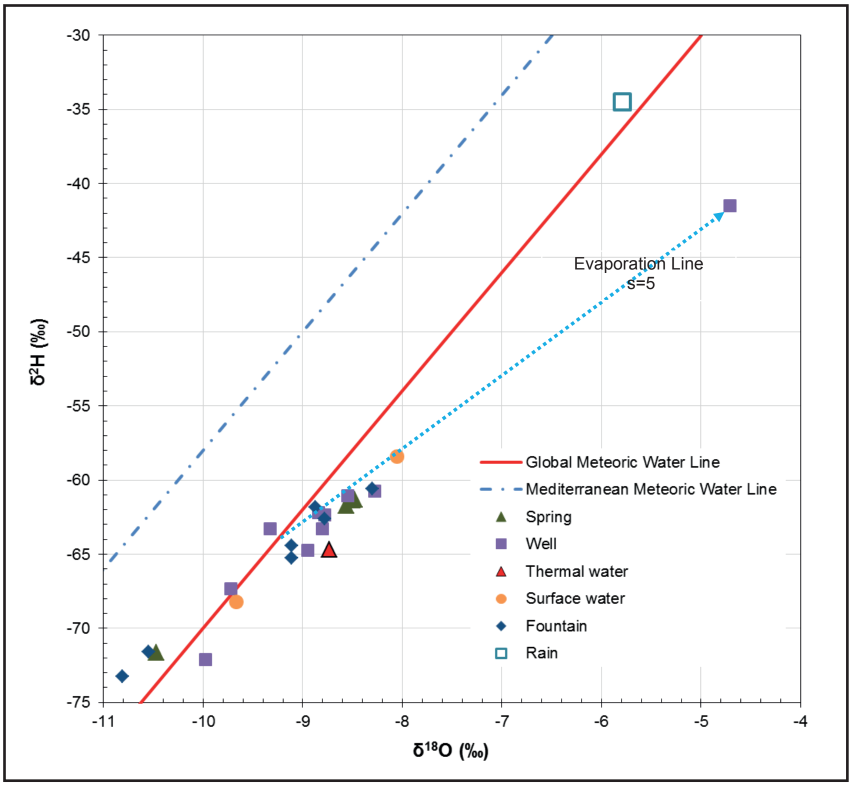

Figure 4- δ^2H vs. $\delta^{18}O$ diagram for May 2012 (wet period). Global Meteoric Water Line is defined by equation $\delta^2H = 8\delta^{18}O+10$ (‰ SMOW) (Craig, 1961), Mediterranean Meteoric Water Line is defined by equation $\delta^2H = 8\delta^{18}O+22$ (‰ SMOW) (Gat and Carmi, 1970).

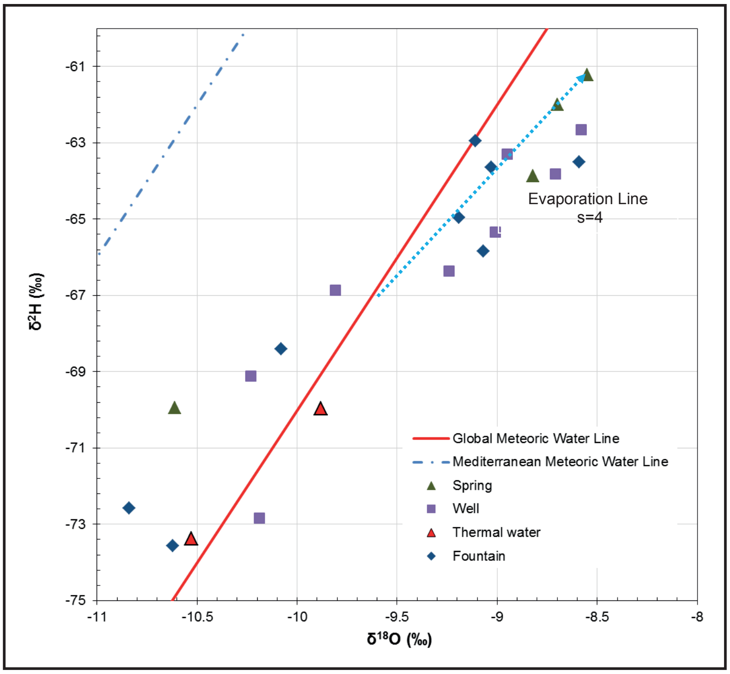

Figure 5- δ^2H vs. $\delta^{18}O$ diagram for September 2012 (dry period). Global Meteoric Water Line is defined by equation $\delta^2H = 8\delta^{18}O+10$ (‰ SMOW) (Craig, 1961), Mediterranean Meteoric Water Line is defined by equation $\delta^2H = 8\delta^{18}O+22$ (‰ SMOW) (Gat and Carmi, 1970).

in Geven village. It was impossible to approach the wellhead during sampling so the sample was collected from a creek formed by the water leaking from the well. As a result, the sample was not only unable to reflect the actual isotopic content of the thermal water but also shows evaporation. This well was also sampled in September 2012, this time from the wellhead. For sampling periods May 2012- September 2012, the difference in $\delta^{18}O$ and δD contents are reported as 1.8‰ and 8.7 ‰, respectively. These differences are far from reflecting seasonal changes, they are rather related to sampling.

δ^2H vs. $\delta^{18}O$ graph prepared by using the stable isotope contents of samples collected in September 2012 reveals out that there is another evaporation line formed for some samples collected from springs, wells and fountains. This time, slope is slightly smaller than the slopes calculated for previous periods (s~4). In this period, samples depleted in heavy isotopes are collected from fountains Şahin and Sekiören villages, thermal well of Dumlupınar University in Geven village and from Gümüşköy village well.

When deuterium excess values obtained throughout three sampling periods are evaluated, the lowest deuterium excess values are observed in samples under evaporation effect and the maximum value is observed in one sample from Şahin village. This sample is enriched in heavy isotopes, doesn't show evaporation effect and its discharge elevation is relatively higher.

3.2. Relationship of Elevation and Oxygen-18 for Precipitation

Oxygen-18 content of precipitation changes with temperature, altitude and latitude. The temperatures drop at higher altitudes and precipitation gets depleted in heavy isotopes. This depletion varies between -0.15 and -0.5 per 100 m rise in altitude for $\delta^{18}O$ (Clark and Fritz, 1997). In the content of this study, it has been aimed to get information about the isotopic character of precipitation falling into different altitudes; however, it was impossible to find enough number of seasonal springs discharging from different altitudes. Therefore, the comments about this subject were carried out by relatively comparing the recharge altitudes of groundwater and thermal water samples. In the light of this information, throughout the basin, the isotopically most depleted samples are Gümüşgölcük artesien well (GG-AR-1), Şahin village spring (SK), Sekiören village fountain (SEK-YAS), Sekiören spring collected previous to pond (SEK-GO), Gümüşköy fountain (GK-CES) and well (GK-

AR-1). These samples are recharged by precipitation from higher altitudes.

3.3. Evaluation of Tritium Data

In this study, besides stable isotopes, the radioactive isotopes of hydrogen and carbon were also utilized. Tritium, which is a short-lived isotope of hydrogen, is formed as a result of the reaction of ^{14}N isotope with cosmic rays. Besides, there is tritium input to the atmosphere as a result of nuclear tests. In groundwater systems, tritium is an excellent tracer since it is part of a water molecule. Because it is radioactive (half-life 12.43 years), it is commonly used to determine the relative age of groundwater (Clark and Fritz, 1997). Concentration of tritium in meteoric waters is reported in Tritium Unit (TU) (1 TU=1 atom ^{3}H /10^{18} atom H). The concentration of tritium, especially in the northern hemisphere, has changed as a result of nuclear tests. Before 1963, the concentrations were about 5 TU and with the tritium input as a result of nuclear tests the concentrations reached to a maximum of 3000 TU. (Mazor, 1991). If the tritium content of precipitation before 1963 is assumed to be 5 TU, then until sampling date (year 2012- 49 years of radioactive decay) the expected tritium concentration in precipitation becomes 0.32 TU. Therefore, when the tritium content of groundwater is interpreted it can generally be said that if groundwater does not contain tritium or contains less than 0.32 TU then the water sampled should have been recharged by precipitation occuring before nuclear tests (year 1963).

According to tritium data (^{3}H) obtained during this study, the tritium content of the samples vary from ~0 TU to 6.11 TU in wet period and from ~0 TU to 7.87 TU in dry period. Accordingly, in the basin there are waters present that are recharged both by precipitation before the start of the nuclear tests (year ~1963) (<0.32 TU) and after (>0.32 TU). Most groundwater samples are recharged by recent precipitation, does not have a high residence tie and they have shallow circulation. The samples from Gümüşgölcük and Kızılcakaya village artesian wells and thermal waters contain very low tritium and they are probably recharged before the nuclear tests. For these samples, detailed interpretations will be done in the following section during the evaluation of carbon-14 data.

During wet period (May 2012), according to the relationship between tritium and δ^{18}O, two spring samples are recharged by recent precipitation falling into higher altitudes (Figure 6). The samples with relatively low ^{3}H content are recharged by precipitation falling into lower altitudes. When all of the samples with shallow circulation (high tritium samples) are examined, it can be said that these samples are recharged by precipitation from different altitudes. Since some of the samples are under evaporation effect (Especially thermal water sample: GE-U), accurate estimations about the relative recharge elevations cannot be done by using δ^{18}O data. During dry period (September 2012), ^{3}H vs. δ^{18}O graph revealed out that the samples having the highest recharge elevation and residence time are the thermal waters (Figure 7). Besides, two groundwater sample with low tritium content (GG-AR-1 and KK-A-DSI) are recharged from different elevations (the recharge elevation of GG-AR-1 is relatively lower). In figure 7, for all samples there isn't any relationship between ^{3}H and δ^{18}O.

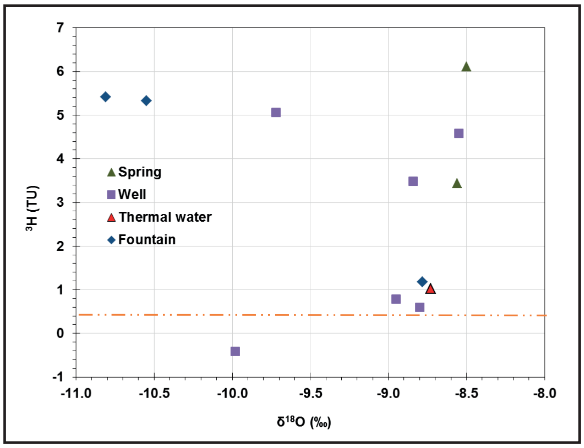

Figure 6- Tritium vs. δ^{18}O for the water samples in wet period (May 2012).

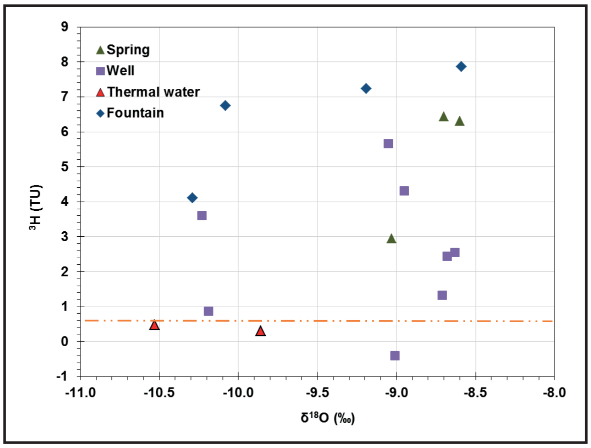

Figure 7- Tritium vs. δ^{18}O for the water samples in dry period (September 2012).

The relationship between tritium and electrical conductivity in wet and dry periods are presented in figure 8 and 9. According to figure 8, ^{3}H and EC are inversely proportional. With the decreasing ^{3}H content EC is expected to increase (with increasing groundwater residence time within the aquifer the amount of dissolved ions also increases). Relatively deep circulated samples have EC values ranging from 400 to 1400 µS/cm. According to Figure 9, shallow and relatively deep circulated waters have similar EC values and there is not any relationship between ^{3}H and EC.

3.4. Evaluation of Carbon-13 (δ^{13}C) and Carbon-14 Data

Within the scope of this work, in the samples having the lowest tritium contents radiocarbon analyses were also carried out to determine the residence times. Radiocarbon method is a standard method allowing dating up to 40000 years before present. This method relies on the measurement of carbon-13 (δ^{13}C) and carbon- 14 (^{14}C) in Dissolved Inorganic Carbon ($DIC = CO_{2(aq)} + HCO_3^- + CO_3^{-2}$). Radioactive isotope of carbon is (Libby half-life 5568±30 years, Cambridge half-life is 5730±40 years) present in the atmosphere and it dissolves in the unsaturated zone until it reaches water table and starts decaying to nitrogen in the groundwater system.

According to table 3, modern carbon contents (^{14}C) of 5 samples range from 8.18 pmc to 77.96 pmc, the highest content observed in Gevrekseydi artesian well and the lowest one observed in the thermal water well located in Geven. **δ^{13}**C contents of groundwaters range between -11.4 ‰ and -14.6 ‰, whereas **δ^{13}**C contents of thermal waters are about -5 ‰. The difference between **δ^{13}**C contents of thermal waters and groundwaters can be attributed to water-rock interaction. In other words, the enrichment in **δ^{13}**C contents, especially in thermal waters, suggests that there is isotopic exchange between water and aquifer material.

Determination of groundwater residence times with ^{14}C method is based on the measurement of the loss of the parent radionuclide, ^{14}C (Clark and Fritz, 1997). Equation 1 is used to calculate the radiocarbon ages of waters.

$$A = A_0 e^{-\lambda t} \qquad \text{(Equation 1)}$$

In Equation 1, A is the measured or observed activity of the sample, λ is the decay constant and t is the time passed after recharge. If the initial radiocarbon activity, A_0 is not assigned correctly, then the above equation would not give accurate results. It is hard to assign a correct value to the initial activity since there are various processes that have an effect upon ^{14}C in water. In addition, the final concentration of ^{14}C in the groundwater is also modified by isotopic exchange as a result of recrystallization and precipitation reactions.

3.4.1 Carbon-13 in the Carbonate System

Clark and Fritz (1997) indicated that carbon-13 is an excellent tracer for the evolution of carbonates in groundwaters. The cause of this is that different carbon reservoirs have different carbon-13 values. The development of Dissolved Inorganic Carbon

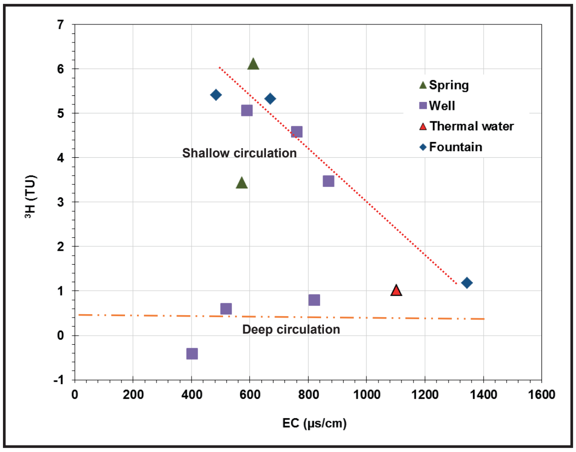

Figure 8- Tritium vs. Electrical Conductivity in wet period (May 2012).

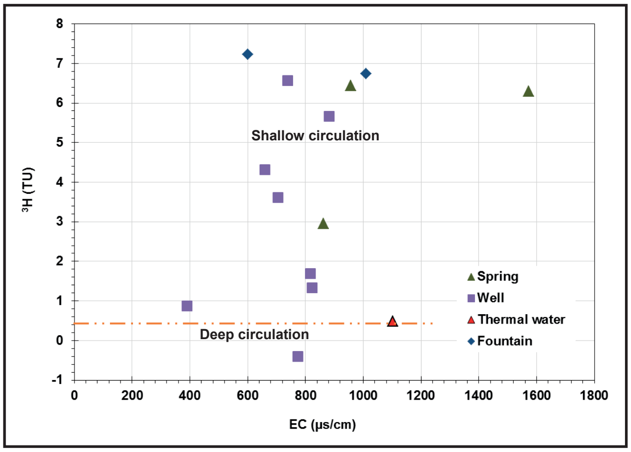

Figure 9- Tritium vs. Electrical Conductivity in dry period (September 2012).

(DIC) and $\delta^{13}C_{DIC}$ begins with atmospheric CO_2. At this point, $\delta^{13}C$ value is approximately -7 ‰ VPDB. Photosynthetic uptake of $CO_{2(atm)}$ cause a visible depletion in $\delta^{13}C$ values. This uptake occurs during CO_2 diffusion from leaf pores and during carbon fixation (transformation of CO_2 to CH_2O) which is carried out by chloroplast of leaves (Clark and Fritz, 1997). The depletion in the amount of ^{13}C differs according to the observed photosynthetic cycle. There are three main known photosynthetic cycles. These are Calvin or C_3 cycle, Hatch-Slack or C_4 cycle and Crassulacean acid metabolism (CAM) cycle (Clark and Fritz, 1997). Calvin cycle is observed in 85% of the plants and $\delta^{13}C$ values of the plants following this cycle is approximately -27 ‰ (Vogel, 1993). At higher temperatures, the plants follow C_4 cycle and $\delta^{13}C$ values are approximately -12.5 ‰ (Vogel, 1993).

3.4.2 Correction of ^{14}C Ages for Carbonate Dissolution

There are different methods to calculate apparent ^{14}C ages and application of these methods are generally decided according to chemical system and the data available. $\delta^{13}C$ mixing model, suggested by Pearson (1965) and Pearson and Hanshaw (1970), was used in order to be able to perform an estimated age calculation according to the data obtained in this study. This model enables using carbonate dissolution in open system conditions together with radiocarbon dilution in closed system conditions (Clark and Fritz, 1997). Every process adding carbon to DIC pool and removing carbon from the pool, affect $\delta^{13}C$ concentrations. The change of DIC in groundwater in one area could demonstrate to what degree carbon-14 concentrations influenced by the addition of dead carbon (Clark and Fritz, 1997). The dilution factor (q) is a number used to prevent factors affecting carbon-14 concentrations to produce false results in age calculation. This factor is demonstrated in the below equation (Equation 2) (Pearson and Hanshaw, 1970).

$$q = \frac{\delta^{13}C_{çik} - \delta^{13}C_{karb}}{\delta^{13}C_{toprak} - \delta^{13}C_{karb}} \qquad \text{(Equation 2)}$$

In Equation 2, $\delta^{13}C_{DIC}$ is $\delta^{13}C$ measured from dissolved inorganic carbon ; $\delta^{13}C_{soil}$ is $\delta^{13}C$ of CO_2 in soil (it depends on the vegetation, C_3 plants -27‰, C_4 plants approximately -12.5‰); and $\delta^{13}C_{carb}$ is $\delta^{13}C$ dissolved in calcite (generally very close to 0 ‰, 2‰ for marine carbonates). Within the scope of the current study, a sample was taken from the aquifer material carbonate rocks which host the groundwater in the area (microcrystalline limestone, close to Ören village) and $\delta^{13}C$ content in this sample was determined as +2.9‰. Thus, only unknown variable during the calculation of q is $\delta^{13}C$ content of the soil which changes according to vegetation cover. C_4 plants mostly grow in tropic and semitropic regions. The dominant vegetation in the basin is generally forest and steppe and these plants follow C_3 cycle predominantly during photosynthesis. According to this, it is appropriate to accept this content as -27‰ for current samples. On the other hand, this value might not be constant from past to present. However, it is difficult to estimate the vegetation in the study area for the last 20,000 years before present. So it should be considered that there would be some uncertainity in calculation of age for samples which are not modern due to the uncertainities in $\delta^{13}C_{soil}$ values. While performing age calculations with carbon-13 correction, if $t_{1/2}$ is taken as 5568 years, then Equation 1 becomes Equation 3 (Clark and Fritz, 1997). Radiocarbon ages were calculated by assuming A_0 as 100 pmc in Equation 3 and these ages are presented in table 3.

$$t = -8035 * \ln\left(\frac{A_t{}^{14}C}{q * A_0{}^{14}C}\right) \qquad \text{(Equation 3)}$$

When the radiocarbon ages presented in table 3 are compared, it can be seen that as the corrections for carbonate dissolution for thermal waters are high, the apparent ages are considerably lower than uncorrected ages. The reason for this is the water-rock interaction during which there is contribution of “dead carbon” from millions of years old carbonate aquifer matrix having a carbon content of 0 pmc. As a result of the contribution of “dead carbon” ^{14}C concentrations measured in the sample are diluted and the ages come up to be older than the actual ages (Ingebridsten and Sanford, 1998). Thus, as carbon 13 content of the sample becomes positive, in other words as the dead carbon contribution increases so as the difference between the corrected and uncorrected ages increases.

It could be understood that the sample obtained from the artesian well in Gümüşgölcük (GG-AR-1) has the highest groundwater residence time without taking high amounts of dead carbon to its system from the aquifer material whereas modern recharge is predominant in the sample obtained from

Gevrekseydi well. The residence time of sample (GG-AR-1) is determined as 11.500 years and the results indicate presence of fossil groundwaters in the basin. Kızılcakaya artesian well has similar duration of stay in underground with thermal water samples so it can be stated that there is hot water mixture to this water in the light of the temperature and chemical data. (Arslan and Celik, 2013). According to the diagram demonstrating the relation between radiocarbon activity and oxygen-18 content, the samples depleted in heavy isotopes have lower modern carbon activities (Figure 10).

4. Conclusions

Utilization of the isotopes having known behaviour in the hydrologic system offers researchers beneficial information. In this study, isotopic features of the surface waters and groundwaters in Köprüören Basin are presented. According to the results, $\delta^{18}O$ and δD contents of some samples show deviations from Global Meteoric Water Line. The $\delta^{18}O$ and δD signature of these samples are modified as a result of evaporation. Evaporation is an expected situation in surface waters. The evaporation lines determined for each different sampling periods have slopes in accordance with the relative humidity in air. The thermal water samples plot along Global Meteoric Water Line and for these samples $\delta^{18}O$ signatures were not modified due to water-rock interaction. The reason for this is attributed to the relatively low wellhead and reservoir temperatures of thermal water samples. In the context of this study, it was impossible to relate $\delta^{18}O$ to altitude and recharge altitude calculations could not be carried out. Therefore, the comments about the subject matter are made on the basis of relative comparisons. Tritium data revealed out that some of the groundwater samples are recharged by recent precipitation, did not stay long in the aquifer and they have shallow circulation. In addition to this, the low tritium contents of thermal water samples and two groundwater samples pointed the existence of waters which entered the system before nuclear tests (before last 50 years) and have relatively long residence times. In order to obtain more information about the residence times of these samples, $\delta^{13}C$ and ^{14}C data are evaluated. For these samples, the apparent ^{14}C ages, corrected against carbonate dissolution, reach up to 11500 before present. Accordingly, these results indicate the existence of fossil (paleo) waters. As a result of water-rock interaction, there is addition of dead carbon to thermal waters and the ^{14}C concentrations of these samples are diluted. Therefore, the correction against carbonate dissolution is considerably high.

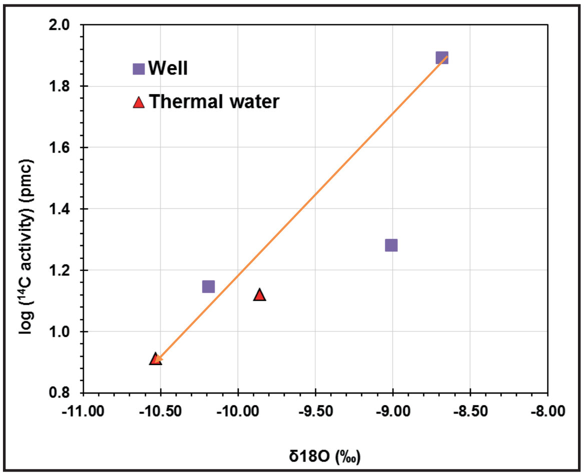

Figure 10- Logarithm of 14C activity (pmc) vs. $\delta^{18}O$ (‰).

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