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INVESTIGATION OF GÜLLÜK (MUĞLA) WETLAND USING STABLE ISOTOPES ($\delta^{18}O$, δD)

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ABSTRACT

Wetlands play an important role in the hydrologic cycle. This investigation was completed to determine the origin of waters and recharge-discharge areas using stable isotopes ($\delta^{18}O$ and δD) which are fingerprints of the water in Güllük (Muğla) wetland. This area is important both economically and in terms of aquaculture environment in Turkey. Sample locations were selected from not only wetlands but also the possible recharge area that consists of karstic springs and streams. EC (Electrical Conductivity) of the waters range between 5080-41000 μS/cm, except streams. $\delta^{18}O$ and δD contents of the samples ranged from -6.00‰ to 0.50‰ and from -29.1‰ to 2.1‰, respectively. In general, samples plotted between Global and Local Meteoric Water line with waters also plotted on the seawater mixing line. The sources of salinity were evaluated by $\delta^{18}O$-Cl in and around the wetland. Streams are under the influence of "Evaporation"; samples from Avşar and Koruköy are under the influence of "Both Evaporation and Seawater Mixing"; İçme and Ekinambarı springs, and Limni Lake are under the influence of "Seawater Mixing"; and Savran spring and Tuzla Lake are under the influence of "Dissolution of Salts-Leaching" processes. The fact that Savran source plotted in this area raises the question of whether the current sea water is the source of salinity. The recharge area of the wetland consists of karstic formations, sea water, streams and precipitation in the Güllük area.

1. Introduction

Wetlands are complicated and very sensitive ecologic locations involving many biological, hydrological and hydrogeological elements. They have a very important place in terms of fresh water supply within the hydrological water cycle. The presence, attributes, quality and potential of water are significant factors directly affecting the wildlife and plant cover in wetlands (Somay and Gemici, 2012). As such for groundwater recharge by wetlands (surface waters filtered by soil and rocks mixing with underground water), hydrogeology, hydrogeochemistry and water-rock interaction are important (Somay and Filiz, 2005). Hydrogeology, hydrogeochemistry and environmental isotopes aid in the determination of water types, recharge-discharge limits, and water storage capacities of wetlands (Somay and Filiz, 2006). The water quality in wetlands is linked to rock types, mineralogy, and distance from the sea, industry-agriculture and settlement areas. Lithology controls major ion exchanges and which minerals saturate the water (Somay and Filiz, 2005). The major/minor ion contents and environmental isotope values of water indicate how waters arrived at which source. There are some hydrogeological and hydrogeochemical studies completed on some important coastal wetland areas in western Anatolia (Gediz Delta, Küçük Menderes Coastal Wetland, Büyük Menderes Coastal Wetland) (Somay and Filiz, 2003; Somay et al., 2008; Somay and Gemici, 2009; Somay and Gemici, 2012). Additionally as the studied region is an important karstic area, there are many hydrogeological and hydrogeochemical studies on karstic areas in the western Aegean and Mediterranean (Öztan et al., 2004; Yüce, 2005; Ekmekçi et al., 2008; Özyurt, 2008; Bayarı et al., 2011; Günay et al., 2015).

One of Turkey's important wetlands of Güllük (Muğla) and Tuzla-Boğaziçi Lake is a significant region contributing to the country's economy with aquaculture in addition to tourism and cultural heritage (Figure 1). The region in the south of Milas county in Muğla also houses an active airport. The Republic of Turkey Ministry of Forestry and Water Management began the Tuzla Lake and Güllük Delta Wetland Management Plan Project and Tuzla Lake and Güllük Delta Wetlands Sub-basin Biodiversity Research Subproject as the area is an important wetland. With depth varying from 0.5-5.0 m covering

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2500 decares, the area covered by Güllük lagoon is linked to Güllük Bay with a canal (Egemen et al., 1999). One of the first and largest fishtraps in Turkey is Güllük Lagoon northeast of Milas-Güllük covering the mouth of Sarıçay, with seawater access from the Aegean Sea through Güllük Bay while freshwater input comes from drainage channels collecting water from tobacco and cotton fields surrounding the trap dug by the General Directorate of State Hydraulic Works (DSI). Topics like whether the chemical balance is preserved or not, which regions the wetland is recharged by and the water-rock interaction have not been determined. The majority of studies in the area have focused on seafood, geography and partial agricultural applications (e.g., Dalman et al., 2006; Demirak et al., 2006; Tuna et al., 2007; Kaymakçı et al., 2010; Yücel-Gier et al., 2013 Kalkan and Altuğ, 2015; Altınsaçlı et al., 2015). Additionally the karstic areas around Milas were studied by Barut et al. (2001), while the geology of the region was studied by Yılmaz et al. (2002) Aksoy and Aksarı, (2008) and Arslan et al. (2013).

Oxygen and hydrogen isotope ratios vary linked to different factors such as precipitation in the region, evaporation amounts and geographic conditions (Clark et al., 1997). Temperature plays an important role in the variation of isotopic ratios. As temperature increases, evaporation increases and increased evaporation leads to depletion of light isotopes and enrichment of heavy isotopes in the ratio. Thus, heavy isotopic compositions are dominant (Clark and Fritz, 1997). Surface and underground water which are not affected by a significant degree of evaporation are located on the global meteoric water line. Spring and summer rains and precipitation at lower elevations have slightly positive $\delta^{18}O$ and $\delta^{2}H$ values above the global meteoric water line. In contrast, autumn and winter rains and precipitation at high elevations have more negative $\delta^{18}O$ and $\delta^{2}H$ values (Coplen et al., 2000). Environmental isotopes in the study area are used to determine distribution of recharge areas, source of water, evaporation rates, mixing rates of seawater, fresh water and geothermal waters and rock-water interactions.

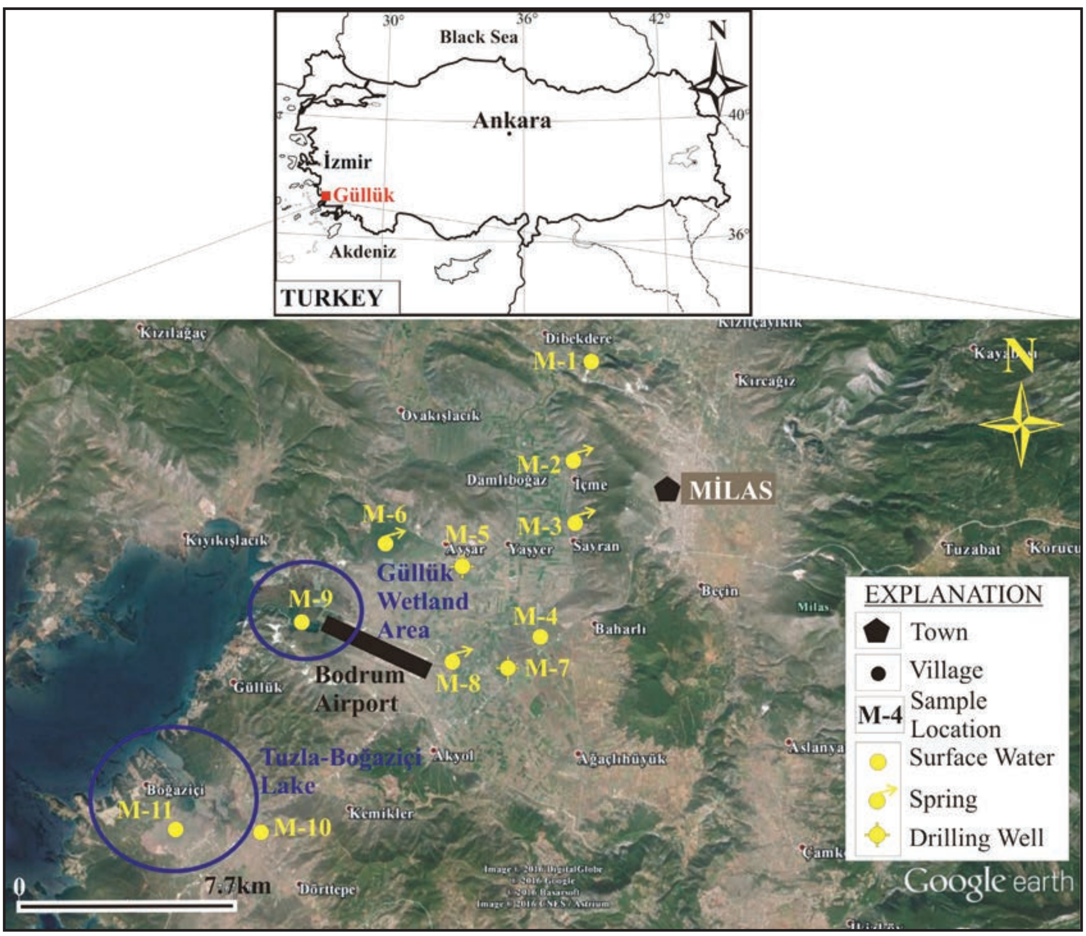

Figure 1- Location of the study area and sample locations.

In this way, the recharge-discharge and water-rock interaction are important in terms of continuity and sustainability of the naturally, culturally and economically important Güllük wetland. Within this study environmental isotope analyses of samples with important representative capacity were completed with the aim of researching the recharge and sources of water within and around the wetland area.

2. Climate Characteristics

The long term meteorological data (1950-2014) were obtained from the Turkish State Meteorological Service linked to the Republic of Turkey Ministry of Forestry and Water Management (Table 1). The lowest monthly mean temperature in the region is 5.5 ºC for the month of January with highest monthly mean temperature of 26.3 ºC for the month of July. The annual mean precipitation amount for Muğla province was measured as 811.3 mm. Using the 64-year meteorological data, the evapotranspiration values for the region were calculated using the "Thornthwaite" (1948) method with the EVAPO (Birsoy and Ölgen, 1991) program (Table 1). According to the Thornthwaite method, the study area has climate type "B3,B'2,s2,b'3 (Humid, Mesothermal, Water deficit in summer and strong, summer evaporation rate: 54%)". The Etp (potential evapotranspiration) was calculated with the method as follows:

$$Etp = 1.6\left(\frac{10t}{I}\right)^{a} \qquad \text{(Equation 1)}$$

In this formula Etp: potential evapotranspiration (mm); t: monthly mean temperature (°C); I: total temperature indice and a: $6.75*10^{-7}\ I^3 - 7.71*10^{-5}\ I^2 + 1.79*10^{-2}\ I + 0.492$. The meteorological data were used in the EVAPO computer program with the Etp formula and the values obtained are shown in Table 1 and from these a "Evapotranspiration Graph" was drawn (Figure 2). In table 1, PE is potential evapotranspiration, CPE is corrected evapotranspiration and ETR is real evapotranspiration. In calculations the soil-moisture reserve (beneficial water reserve) was conceptually taken as 100 mm. When the table is examined, in January, February and March precipitation appears to be greater than Etp and as a result Etp is equivalent to Etr (real evapotranspiration). Some of the surplus precipitation feeds rivers while some recharges groundwater. In the months of April, May and June, the water shortage occurring due to precipitation being less than Etp is compensated by the soil-moisture reserve conceptually assumed to be 100 mm. Thus from June to October, an agricultural water shortage (water deficit) occurs. Between July to October, the Etr value is written as the mean monthly precipitation values for the region. As precipitation is once again greater than Etp in November and December, it is equal to Etr. Here the surplus precipitation recharges the consumed soil-moisture reserve. The remaining precipitation surplus feeds surface and groundwater.

Table 1- Thornthwaite Water Balance Table (T: temperature-°C; TI: temperature indices; PE: potential evapotranspiration-mm; CF: Correction Factor; CPE: Corrected PE-mm; P: precipitation-mm; SC: Storage Change; S: Storage; ETR: Real evapotranspiration (mm); WD: Water Deficiency; EW: Excessive Water; RO: Runoff-mm; MR: Moisture Ratio).

Data	January	February	March	April	May	June	July	August	September	October	November	December	Total
T	5.5	6.1	8.5	12.5	17.6	22.9	26.3	26.1	21.7	15.9	10.5	7.0	
TI	1.2	1.4	2.2	4.0	6.7	10.0	12.3	12.2	9.2	5.8	3.1	1.7	69.8
PE	10.9	12.9	21.9	40.6	70.1	106.7	133.1	131.5	97.9	59.6	30.7	16.1	732.2
CF	0.9	0.8	1.0	1.1	1.2	1.2	1.3	1.2	1.0	1.0	0.9	0.8	
CPE	9.3	10.9	22.6	44.7	86.2	132.3	166.4	153.9	101.9	57.2	25.8	13.4	824.5
P	235.3	174.7	117.6	66.3	48.8	22.5	7.5	7.2	17.0	66.5	136.8	259.0	811.3
SC	0	0	0	0	37.4	62.6	0	0	0	9.3	90.7	0	
S	100	100	100	100	62.6	0	0	0	0	9.3	100	100	
ETR	9.3	10.9	22.6	44.7	86.2	85.1	7.5	7.2	17.0	57.2	25.8	13.4	386.8
WD	0	0	0	0	0	47.2	158.9	146.7	84.9	0	0	0	437.66
EW	226.0	163.9	95.0	21.6	0	0	0	0	0	0	111.0	245.7	863.1
RO	113.0	194.9	129.4	58.3	10.8	0	0	0	0	0	55.5	178.3	740.3
MR	24.3	15.1	4.2	0.5	-0.4	-0.8	-1.0	-1.0	-0.8	0.2	4.3	18.4	

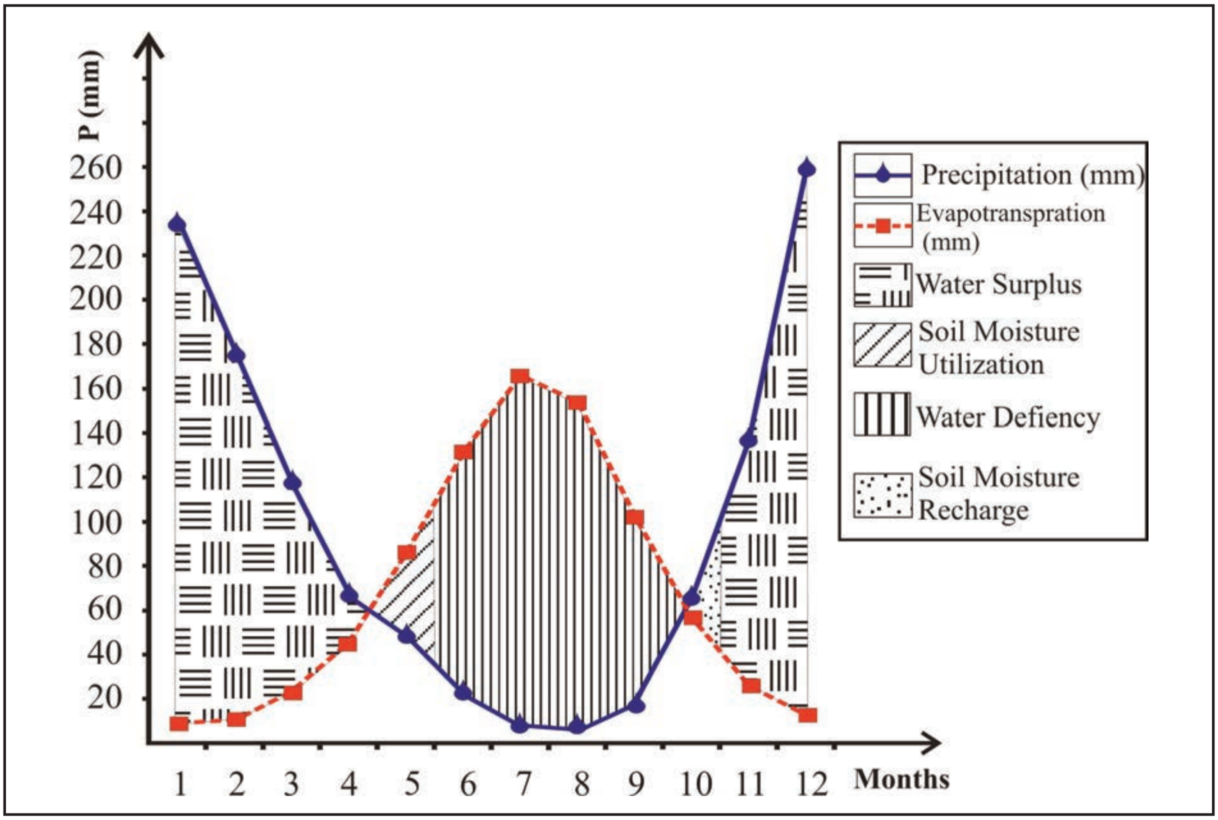

Figure 2- Thornthwaite graph for the study area.

3. Sampling and Analysis

In March 2014, 11 water samples were taken from the study area; 5 surface water samples from rivers and lakes, 4 from springs and 2 from underground water in drill holes (Figure 1). At all these points, water temperature, electrical conductivity (EC) and pH measurements were completed with a WTW brand multimeter device and water was sampled for oxygen-18 ($\delta^{18}O$) and deuterium (δD) analyses. Samples were collected in 50 ml PE plastic bottles and were not filtered.

$\delta^{18}O$ and δD isotope analyses were completed with a GVI Optima isotope mass spectrometer (SIRMS) at California University Davis Stable Isotope Laboratory. Vienna Standard Mean Ocean Water (VSMOW) was used as standard and the measurement sensitivity for this standard was determined as 0.25‰ for $\delta^{18}O$ and 3‰ for δD.

4. Geological and Hydrogeological Characteristics

The study area is located at the SW of the Menderes Massif at the contact with the Likya Nappes (Figure 3). There are three stratigraphic sequences described in the region. These are autochthonous Menderes Massif rocks, allochthonous emplaced Likya Nappe rocks and the young sediments overlying these two rock assemblages (MTA, 2002).

From older to younger the units forming the lithologies in the Menderes Massif comprising the bedrock are; metamorphic basement, Milas formation and Kalınağıl formation (Barut et al., 2001). The metamorphic basement comprises gneiss, schist, quartzite and marbles. The age of the basement rocks was estimated to be Precambrian by Akat (1975). The clayey schist, mica schist, chlorite schist, quartzite, calcschist and marble lenses in this unit are impermeable. Large areas with transitions from marbles to schists may be assessed as local karstic aquifers (Eroskay et al., 1992). However, in general schist and quartzite is impermeable basement (Barut et al., 2001). With broad distribution in the study areas, the concordant Milas Formation above the schists comprises dolomitized limestone (Eroskay et al., 1992). Generally these are permeable and have very karstic character. Karstic springs emerge from the impermeable schist contact at the base of

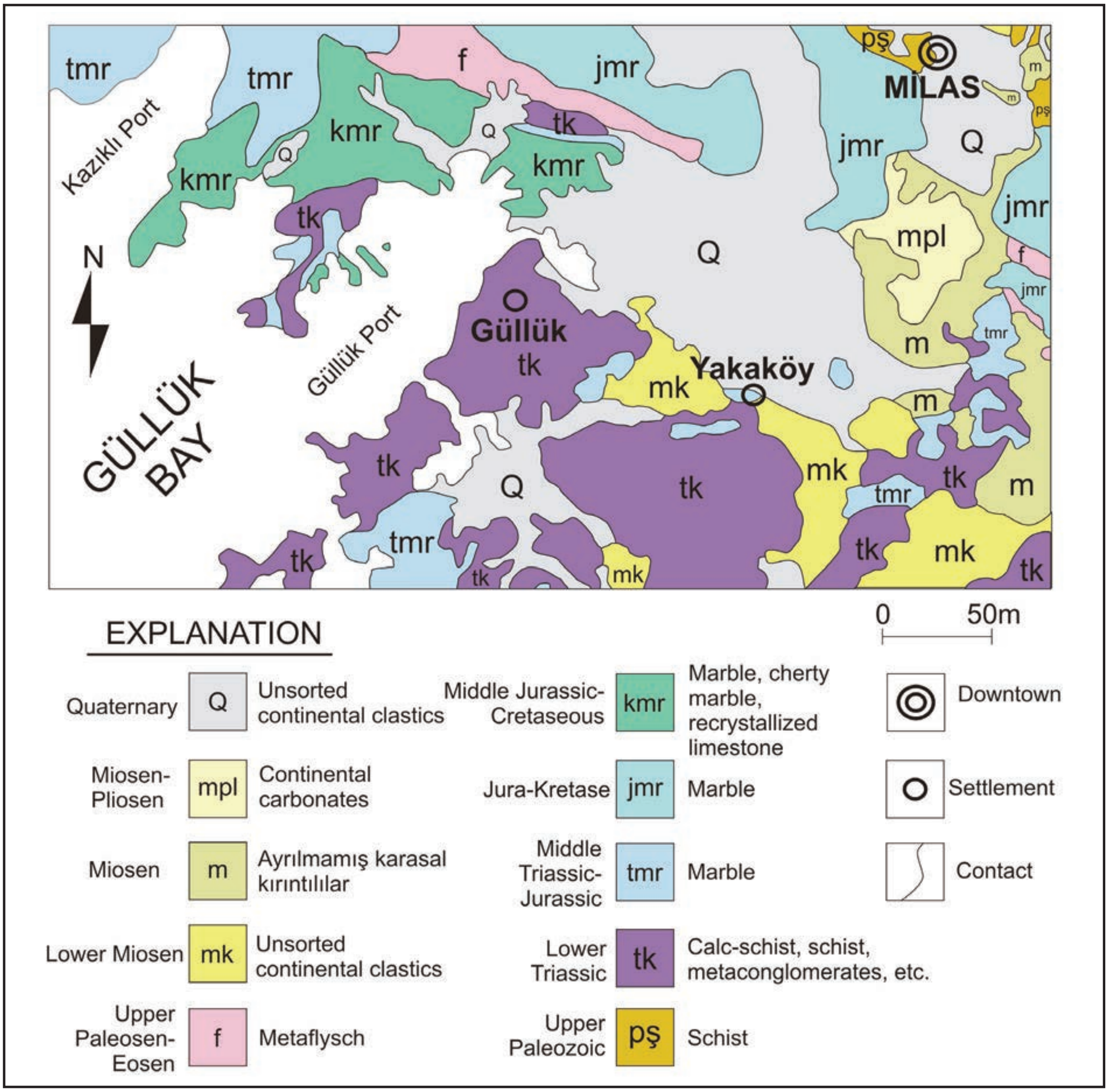

Figure 3- General geological map of the study area (MTA, 2002).

the formation (Barut et al., 2001). The Kalınağıl formation (Eroskay et al., 1992) overlies the Milas formation and is counted as cover on the Menderes Massif and the uppermost unit in the autochthonous sequence. The age of the formation was determined as Maastrichtian-Paleocene (Çağlayan et al., 1980) or Late Paleocene (Akat, 1975). Located at the top of the autochthonous sequence, the formation comprises breccia-structured red limestones, and cherty micritic limestone levels that have karstic permeability. The shale, marl and siltstone levels found at the upper levels of the formation are impermeable. The regions where the limestones from lower levels are exposed have karstic structure. As a result they may be accepted as locally permeable in terms of hydrogeology (Barut et al., 2001). The overthrusts Likya Nappes are internally organized. From bottom to top, this sequence starts with clastic sediments and continues with limestones and repeated clastics above. From younger to older this allochthonous sequence comprises the Gökova formation, allochthonous limestones, Güllük formation and tectonic melange (Barut et al., 2001). The Güllük formation is the lowest in the allochthonous sequence. It comprises initially conglomerate followed by sandstone, shale layers and limestone lenses of varying sizes (Barut et al., 2001). The age of the Güllük formation is Late Permian-Early Triassic (Çağlayan, 1980). Due to its lithological properties, it is generally impermeable. It forms a barrier to underground water movements (Eroskay et al., 1992). In sections near the base of the formation, the limestone under sandstone and shale has karstic character. In the study area the Kıyıkışlacık, Ekinambarı and Yaykın springs emerge from karstic limestone (Barut et al., 2001). According to fossil finds, the age of the sediments is Late Triassic-Liassic (Akat, 1975). According to Barut et al. (2001), the allochthonous sequence above the Güllük formation is a permeable unit. The transitional surfaces with the Güllük formation are impermeable. Levels transformed to dolomite and calcites are permeable and have karstic character. This sequence is composed of rocks such as conglomerate, sandstone, shale, mudstone, limestone, etc. (Barut et al., 2001). The Yatağan formation is formed of lacustrine and river sediments comprising gray, cream-colored sandstone, conglomerate, siltstone, marl, claystone and limestone with occasional coal beds (Barut et al., 2001). These Neogene sediments are covered with alluvium in Milas plain between Ekinambarı and Ağaçlıhöyük. In this formation, a neo-autochthonous sequence, the clays, marls and coal levels are impermeable. There are sorted sandy and pebble levels forming generally locally impermeable cover sediments (Barut et al., 2001). In the study area Quaternary-age alluvium and slope debris are most common on plains between Milas, Ekinambarı, Savran and Hisarcık-Ovakışlacık. Due to active tectonism and linked uplift in the study area, depression areas are commonly filled with broad and thick alluvium sediments (Barut et al., 2001). The alluvial cover is generally permeable. However, upper levels in these sediments containing clay have impermeable character. Karst is observed within slope debris along the Milas-Bodrum road. As a result, in terms of hydrogeology, the alluvium and slope debris are generally accepted as being permeable (Barut et al., 2001).

5. Results and Discussion

The EC values of water samples from the study area were generally very high with values varying from 5080-41000 μS/cm, apart from the Sarıçay-Dibekdere (M-1) sample in the north and the Mazıçayı (M-10) sample in the south (Table 2). The highest value was measured in Tuzla Lake in the south of the study area. This value was close to the EC value of 50000 μS/cm measured in seawater during the study by Barut et al. (2001). Another lake forming an important element of Güllük wetland, Limni Lake, had EC value recorded as 15330 μS/cm. The mean EC value of karstic springs in the basin was 17310 μS/cm.

The pH values of waters in the study area varied from 7.27 to 9.15. Sodium concentrations had a wide interval from 18-11450 mg/l. Calcium amounts were 34-435 mg/l, while Mg amounts were 6-920 mg/l. The dominant anion in the region was Cl and distribution was 15-19600 mg/l. Apart from surface waters, the remaining water samples were Na-Cl water facies type according to IAH (1979) classification.

In a study by Barut and Gürpınar (2005) based on Cl values, the contribution of seawater to karstic springs in the region was calculated as 13% in Ekinambar and Avşar, 35% in Savran and 37% in İçme. This indicates that moving from the sea toward inland, the contribution of seawater increases.

The $\delta^{18}O$ and δD values of samples taken from the study area were between -6.00‰ to 0.50 ‰ and -29.1 ‰ to 2.1 ‰, respectively (Table 2, Figure 4).

Using the formula $d= \delta D-8*\delta^{18}O$, the deuterium excess for samples from the study area was calculated to vary from 6.49 to 18.87 ‰ (Table 2). When the deuterium excess is examined, the samples with lowest deuterium excess had evaporation effects (M6, M10, M11). The highest deuterium excess was from a sample taken from Koruköy dug-well (M7); it was depleted in heavy isotopes compared to other samples and determined to be a sample discharging from higher elevations with no evaporation effect. As given in table 2, when the spring discharge elevation is examined, it is noted that springs discharging from higher elevations are depleted in heavy isotopes. Samples placed along the Global Meteoric Water Line (GMWL: $D=8*\delta^{18}O+10$; Craig, 1961) and the Mediterranean Meteoric Water Line (MMWL: $\delta D=8x\delta^{18}O+22$; Gat and Carmi, 1970). In terms of representing the region, the Local Meteoric Water Line (LMWL: $\delta D=8x\delta^{18}O+14$; Barut et al., 2001) calculated from precipitation in the region was used. The samples with relatively more negative values on the diagram are probably fed from more continental and higher elevations. In light of this knowledge, the most depleted samples in terms of heavy isotopes in

Table 2- Temperature, electrical conductivity and environmental isotope values from the study area (*Sea water values taken from Barut et al. (2001)).

Sample	Location	Distance from Sea (km)	Elevation above sea level (m)	T (°C)	pH	EC (μS/cm)	Cl (mg/l)	δD (‰)	$\delta^{18}O$ (‰)	D – excess (‰)
M-1	Sarıçay-Dibekli	14	27	12.7	8.07	276	15	-28.7	-5.47	15.05
M-2	İçme Spring	12	16	20.1	7.41	18830	6900	-20.5	-4.31	9.97
M-3	Savran Spring	11	13	20.0	7.60	19240	8100	-19.8	-4.13	-1.89
M-4	River-Avşar	9		21.2	7.92	17250	6450	-21.7	-4.33	14.02
M-5	Drilling Well-Avşar	7		21.1	7.35	7190	2600	-24.0	-4.88	13.24
M-6	Avşar Spring	4	2	26.2	8.18	7480	2750	-14.5	-2.63	12.97
M-7	Dug Well-Koruköy	9		19.2	7.27	5080	1650	-29.1	-6.00	15.07
M-8	Ekinambarı Spring	7	11	17.3	7.60	13860	6100	-22.6	-4.60	6.49
M-9	Limni Lake	1		21.2	8.19	15330	6750	-21.8	-4.37	18.87
M-10	Mazı Stream	5		16.5	7.80	799	71	-23.9	-4.24	14.22
M-11	Boğaziçi-Tuzla Lake	3		17.2	8.34	41000	19600	2.1	0.50	13.07
Sea*	Sea water					50000		9.9	1.30	-0.50

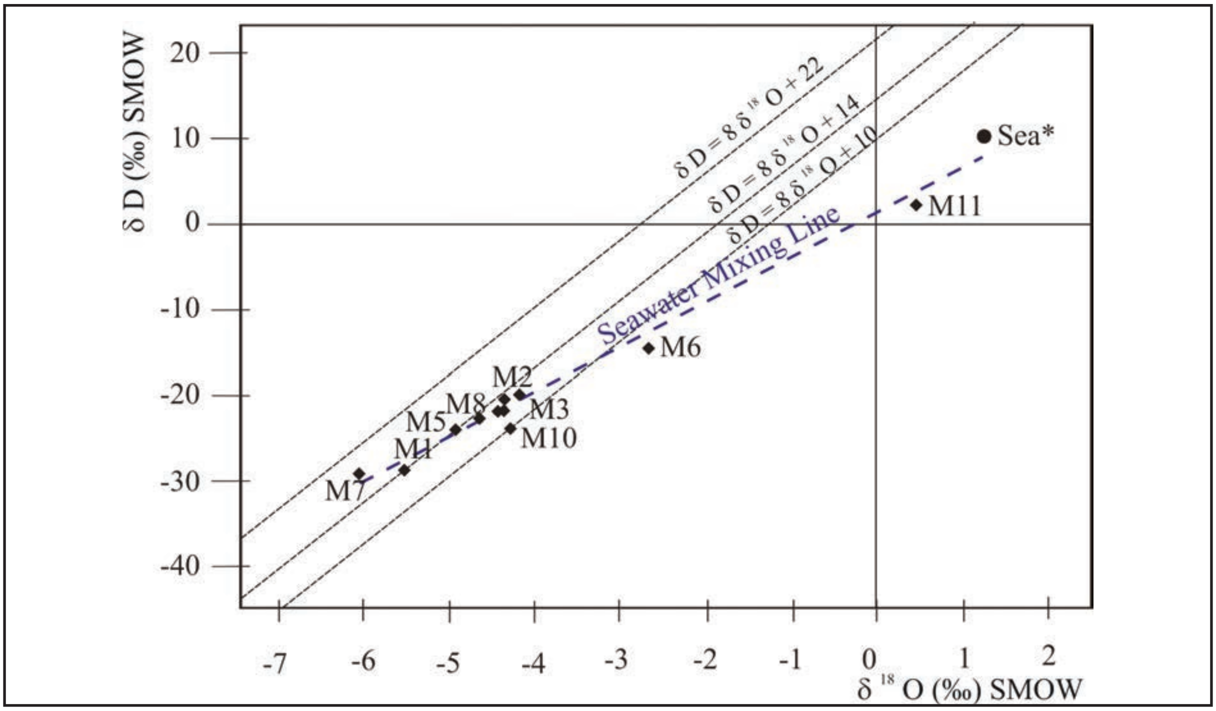

Figure 4- Relationship between $\delta^{18}O$ and δD.

the study area are Koruköy dug-well (M7) and Sarıçay River (M1), with these fed by precipitation falling at higher elevations compared to samples from other locations.

The M6, M10 and M11 samples from the region deviated from the meteoric water line (Figure 4). This deviation may be due to different processes such as evaporation, condensation and water-rock interaction, or CO_2 effects (Clark and Fritz, 1997; Mook, 2001). As mentioned by Clark and Fritz (1997) and Coplen et al. (2000), mixed waters are located on a line with lower slope under the meteoric line. To identify which of these processes caused the deviation, the Cl- $\delta^{18}O$ diagram recommended by Mook (2001) was used for the study area (Figure 5). The sample closest to the fresh water end component was sample M1. Accordingly the dominant processes are shown in figure 5.

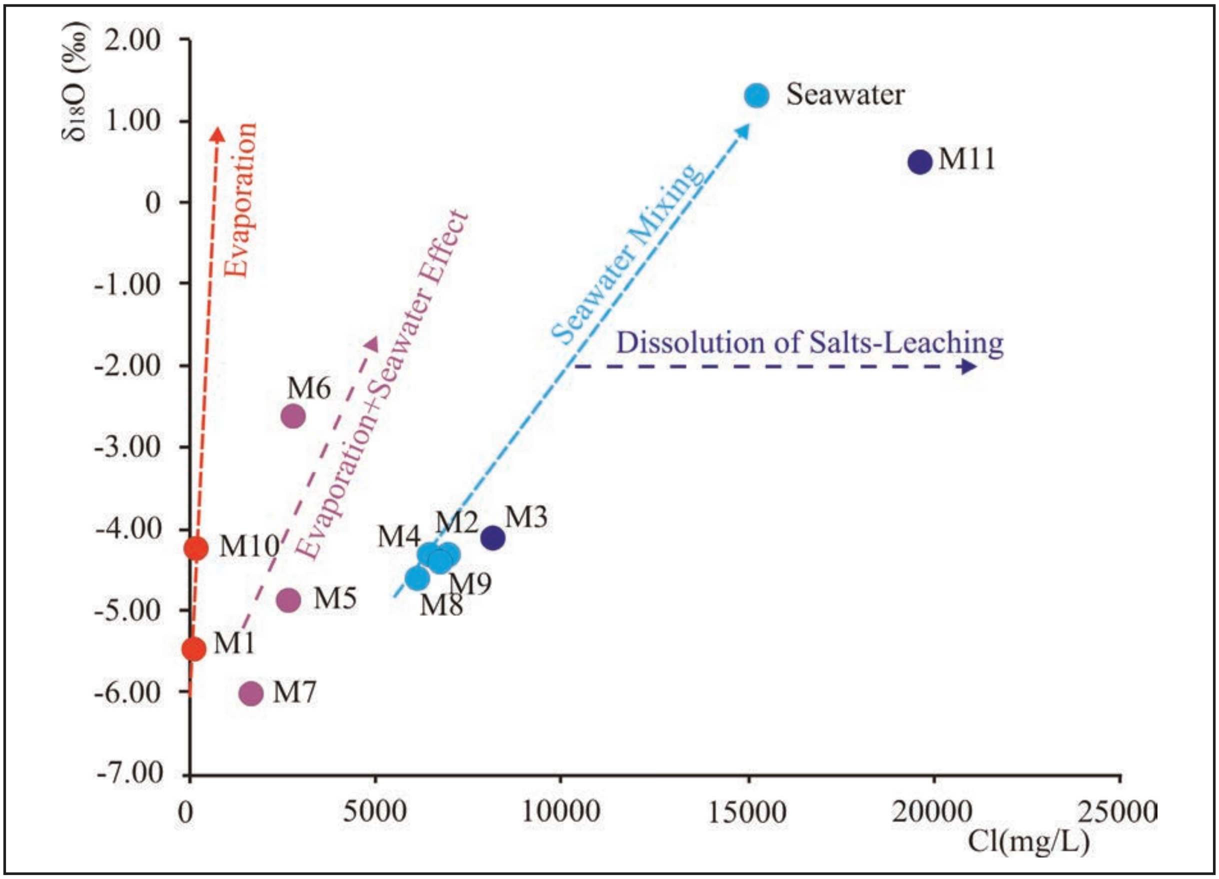

Figure 5- Relationship between Cl and $\delta^{18}O$.

Sea water with nearly 14000 mg/l Cl content and 1.3‰ $\delta^{18}O$ isotope values is located at the top portion of the graph. Relatively more fresh waters with Cl varying from 15-71 mg/l and $\delta^{18}O$ isotopic ratios varying from -5.47 to -4.24 ‰ are located in the left lower corner of the graph. According to figure 5, the surface waters from Sarıçay River (M1) and Mazıçay (M10) are more affected by "evaporation"; samples from Avşar drill hole (M5), Avşar spring (M6) and Koruköy dug-well (M7) are affected by "both evaporation and seawater mixing"; İçme spring (M2), Avşar drainage channel (M4), Ekinambarı spring (M8) and Limni Lake (M9) are affected by "seawater mixing"; and Savran spring (M3) and Tuzla Lake (M11) samples are affected by "dissolution of salts-leaching".

6. Conclusions

Environmental isotope research was completed on one of Turkey's most important aquaculture areas of Güllük wetland. Limni Lake and surrounding karstic springs forming the Güllük wetland comprise a salt-water ecosystem. Seawater continuously advances toward the interior sections of the limestone and feeds İçme and Ekinambarı springs and the lakes (Figure 6). According to Erol (1991), in the last 4000-5000 years a total of 3-4 m uplift has occurred along coasts in Western Anatolia. Additionally, according to Ekmekçi et al. (2008), due to the saltwater wedge geometry in karstic aquifers commonly observed on the south coasts of Turkey and irregular variation of sea levels linked to paleoclimatic conditions, the estimation of equations developed for isolated aquifers is generally difficult. The seawater contribution to spring discharge 11-12 km inland may be explained in this way. The Savran spring discharging 11 km from the sea does not appear to support the current seawater mixing model. Savran spring and Tuzla Lake were defined within the "dissolution of salts-leaching" area and have brine character. The results of comparing analyses from the early 2000s with the isotope analyses of the same springs in this study showed no significant change in the $\delta^{18}O$ and δD values of İçme and Savran springs and they appear stable.

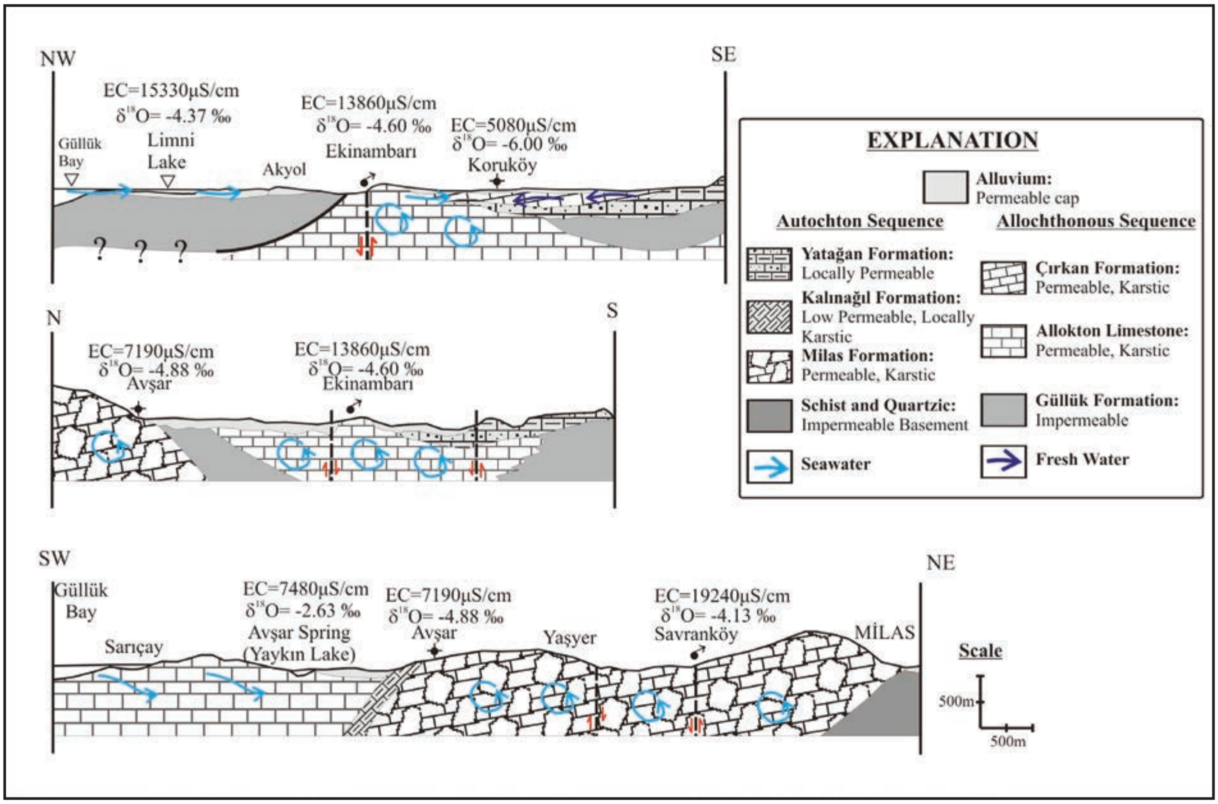

Figure 6- Water circulation model for the study area (Cross sections taken from Barut et al., 2001).

Other sources recharging the wetland are Sarıçay and Mazı Çayı freshwater springs. According to isotope values, these are recharged from high elevations and generally affected by evaporation. The water from Avşar and Koruköy are affected by both seawater mixing and evaporation. Though Koruköy waters, especially, were salty, based on the $\delta^{18}O$ and δD values as it is recharged from the NE Çırkan Formation and relatively high sections, mixing with fresh water is predicted (Figure 6).

Different karstic formations, current and non-current seawater, freshwater streams and precipitation ensure the Güllük wetland is recharged. Currently both fresh and salt water ecosystems appear to be balanced, but in the future the sustainability of these ecosystems should be monitored.

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