

Turkish Journal of Earth Sciences

http://journals.tubitak.gov.tr/earth/

Turkish J Earth Sci (2021) 30: 38-58 © TÜBİTAK doi:10.3906/yer-2005-11

Hydrogeochemical fingerprints of a mixohaline wetland in the Mediterranean: Güllük coastal wetland systems- GCWS (Muğla, Turkey)

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Received: 10.05.2020	•	Accepted/Published Online: 27.08.2020	٠	Final Version: 15.01.2021	
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Abstract: The Güllük coastal wetland system (GCWS), which is located at the contact point of the Menderes Massif and Lycian Nappe, consists of both brackish karstic [Güllük Lagoon wetland (GLW)] and saline [Boğaziçi-Tuzla (Bargylia) coastal wetland (BTW)] ecosystems in western Turkey, and is under protection as a national wetland of importance. This area is important for its unique wetland features, aquaculture, tourism, agriculture, Bodrum airport, and Güllük port facilities. The aim of this study was to evaluate the GLW and BTW, both hydrogeologically and hydrogeochemically, for the first time together. The mixohaline GCWS is recharged from precipitation, streams, and brackish karstic springs. The electrical conductivity (EC) values of Limni Lake and the Tuzla salt pan were measured as 15,330 and 41,000 µS/cm, respectively. The EC value of the brackish karstic springs was ~17,310 µS/cm. From the coast to inland, the mixing ratio increases to a maximum of 45% in Savranköy Spring, which discharges from the contact point between Milas Formation and alluvium. The relationship between Na-Cl, SO₄-HCO₄, and Mg/Ca-Cl showed a weathering by ion exchange and/or seawater intrusion process. All of the groundwater samples comprised NaCl water. In parallel with these results, the diagrams of Gibbs et al. supported the same seawater intrusion phenomena. Brackish karst springs first roseand then fell below sea level with epirogenic movements during the geological period, and therefore, karstification progressed. The samples were oversaturated with calcite, dolomite, and quartz, whereas they were undersaturated with gypsum and halite. The Al, Cu, and Zn values of some of the water samples exceeded the tolerance limit of aquatic life standards. When the samples were evaluated in terms of irrigation water, brackish springs, and streams at Avşar and located near the aquaculture farm, Lake Limni and saltpan had a harmful effect on the plants due to their high Na concentration. These results suggested that the wetland was vulnerable because it was both in a sensitive karstic and a lagoon area. Hydrogeological protected zones should be determined to ensure the sustainability of groundwater resources and provide the economy of the country.

Key words: Wetlands, hydrogeochemistry, hydrogeology, Güllük, Mediterranean, Turkey

1. Introduction

Wetlands are ecologically sensitive areas that have been home to the most important civilizations throughout history. Providing necessary water and nutrients for the survival of humankind and the wide variety of plant and animal species within them have made wetlands important throughout human history. Only 2.5% of the water on the Earth is freshwater (Shiklomanov, 1993), comprising 30% groundwater and 1% surface water. The remaining amount water is in the form of glaciers and ice caps, which cannot be used. Since water is necessary for humanity, freshwater areas are of great importance. These freshwater areas include lakes, rivers, swamps, and groundwater associated with these surface waters. In this context, Wetlands are of great importance in terms of supplying freshwater for the future. Wetlands are also important for controlling climatic changes in various parts of the world, which

affect global climate change. According to Ramsar (2004), wetlands are areas of marsh, fen, peat land, or water, whether natural or artificial, or permanent or temporary, with water that is static or flowing, fresh, brackish, or salt, including areas of marine water, the depth of which at low tide does not exceed 6 m. From this definition, it can be seen that wetlands are of great importance in the hydrological water cycle. Wetlands are places where surface water interacts with groundwater. In studies related to wetlands, only surface waters and surface water recharge basins (hydrological basin) are generally taken into consideration. However, not only surface water, but also groundwater, is effective in wetlands. In some karstic regions, groundwater is more dominant than surface water as a water source. If groundwater is not used sustainably, it may cause a damage or destruction of existing wetlands. As a result, the wetland then loses its function, such as



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its interaction with the associated groundwater systems. In parallel to that, if the sustainability of wetlands is not ensured, a decrease in groundwater potential may be observed.

The 3 types of wetlands can be classified according to geographical situations as:

- · Coastal wetlands
- \cdot Inland wetlands
- · Human-made wetlands

There have been many studies in recent years about ornithological and floral/faunal studies, as well as hydrogeological and hydrogeochemical studies, of both coastal and inland wetlands in Turkey (e.g.,coastal wetlands: Somay and Filiz, 2003; Somay et al., 2008; Somay and Gemici, 2009; Demirel et al., 2011; Somay and Gemici, 2012; Demir Yetiş et al., 2014; Aydın et al., 2015; Somay, 2016. e.g., inland wetlands: Ekmekçi, 1990; Camur et al., 1997; Samsunlu et al., 2002; Yalcin et al., 2007; Bozdağ and Göçmez, 2011; Bayari and Yildiz, 2012; Şener et al., 2013; Karakuş et al., 2017; Varol and Köse, 2018; Okan and Güven, 2019; Davraz et al., 2019).

Coastal lagoons and estuaries represent coastal water bodies formed during rising sealevels, which were particularly high during the Early Holocene (12,000-8000 years ago) and slowed down some 6000 years ago (Kjerfve, 1994). According to Gönenç and Wolflin (2005), coastal lagoons support highly valued natural services. Looking at the environment we are in, Mediterranean lagoons are, in large part, areas of shallow, coastal water, wholly or partially separated from the sea by sandbanks, shingle, or less frequently, rocks (Zaldivar et al., 2008). Water quantity and quality in a lagoon is influenced by the rate at which the lagoon loses or gains water from evaporation, precipitation, groundwater input, surface runoff, and exchange with the ocean (Allen et al., 1981). In addition to being more productive areas than the seas, lagoons are also rich in biodiversity due to their broad spectrum of water quality (Özdemir et al., 2013).

More than 100 lagoons are found along the Mediterranean coastline, but very little hydrological and biological data of most of these ecosystems are available (Pérez-Ruzafa et al., 2011).

The objective of this study was to identify the hydrogeological and hydrogeochemical properties of not only mixing waters in lagoons, but also waters in the hydrological basin of the wetland. In this study, the Güllük and Boğaziçi-Tuzla wetlands were studied together for the first time and evaluated hydrogeologically and hydrogeochemically. Because of the economic contribution of the lagoons to Turkey, it is very important to study them in detail in terms of their sustainability.

2. Study Area

2.1. Location

The Güllük coastal wetland system (GCWS) (Figure 1), which is one of the most important wetlands in Turkey,

¹ www.milas.gov.tr

is in a critical region that contributes to the national economy through its aquaculture, as well as tourism and cultural heritage (Somay, 2017).

The GCWS is consists of the Güllük Lagoon wetland (GLW) and Boğaziçi-Tuzla (Bargylia) coastal wetland (BTW). The BTW and GLW were first identified as an important bird and biodiversity area in 2001. In 2019, the National Wetlands Commission of Turkey declared the BTW was declared a national wetland of importance. The town of Güllük is a triple-function coastal settlement comprising tourism, fishing businesses, and a mineexporting port (Soykan, 1997). According to Köymenoğlu (2013), this region has had a share of 10% of the marine fish production of Turkey since 1986. On the other hand, according to the 2015 records, there are a total of 181 projected earthen pond facilities around the GLW. Considering that the daily water exchange in the ponds will be half the volume of the pond, 834,231,5 m³ of the daily water demand will occur (Tezel, 2015). Increasing secondary residences in the GLW and surrounding area, relocation of Port Güllük from the city center and constructing it near the GLW, the presence of the Bodrum Airport, disposal of the domestic wastewater of the Milas settlement unit after treatment and discharge to the GLW via Sarıçay, the impact of illegal fishing in the sense of fisheries, and the continuation of all of these negative activities is a threat to the future of the GLW (Özdemir et al., 2013; Demirak, 2003). The GLCW covers an area of 1180 ha. According to Milas District Governorate 2019¹, the BTW covers 380 ha and is home to about 3000 flamingoes each year. A total of 4692 birds belonging to 116 different bird species, including 29 water birds, 9 predators, and 78 songbirds have been identified in the GLCW (Bavrak et al., 2013). Some of the fauna species in the GLW are juniper, red pine, pistachio, clematis, buttercup, poppy, and reed. Phragmites australis is a common reed species (Dokuyucu, 2019). There are 14 aquatic invertebrate taxa, 23 aquatic invertebrate taxa, 17 zooplankton taxa, 34 phytoplankton taxa, and 56 macroscopic wetland vegetation taxa (Bayrak et al., 2013). In the GLW, there are 387 plant taxa, which are both aquatic and terrestrial (Dokuyucu, 2019).

The GLCW has been reviewed separately using different disciplines in previous studies (e.g., Eroskay et al., 1992; Barut and Gürpınar, 2005; Barut et al., 2015; Altınsaçlı et al., 2015a; Altınsaçlı et al., 2015b). Since these wetlands form a single ecosystem, in this study, they were evaluated as a coastal wetland system for the first time. According to the classification of Kjerfve (1994), the GLW is a restricted lagoon due to its parallel position to the shore and the fact that is has more than one inlet channel. According to the Ramsar wetland classification, the GLW is defined as coastal brackish/saline lagoons (Code: J) and the BTW is defined as both permanent shallow marine



Figure 1. Location and sample map of the study area.

water less than 6 m deep at low tide, which includes sea bays and straits (Code: A) and intertidal salt flat (Code: G). On the other hand, the GLW comprises brackish karstic springs. Hence, it can be classified as a karst and other subterranean hydrological system for coastal areas (Code: Zk(a)). The GLCW covers an area of 1180 ha. According to Milas district governorate data (2019), the BTW covers 380 ha, and the GLW consists of approximately 800 acres of lake area in a 250-ha swamp area.

2.2. Hydrological features of the GLCW system

The GLW is in an alluvial area and has karstic springs of brackish water [it consists of mesohaline and oligohaline with salinity ranging between 0.5‰ and 18‰, according to the classification of Beadle (1958)]. Sarıçay passes through İçme, Savranköy, and Yaykın karst springs until reaching Limni Lake (Figure 2). The Ekinambarı karst spring is connected to Limni Lake by a drainage channel. Moreover, this spring is also linked to the wetland. Limni Lake is recharged by a small seasonal stream and The General Directorate of State Hydraulic Works (DSI) drainage channel. The material carried by the drainage channel causes Limni Lake to become shallow quickly. Limni Lake has an area of 68 ha and its average depth is between 1 and 2 m (Egemen et al., 1999). Mixing with Sarıçay Stream, brackish karstic spring waters, and seawater result in high salinity and this situation provides more biodiversity in and around the GLW.

The hydrological recharge area of the BTW consists of the Kemikler, Dörttepe-Kemer-Tepecik villages in the southern part of the GLW. The stream that comes from Dörttepe-Kemer-Tepecik village, cuts the İzmir-Bodrum road upright and reaches the BTW. On the other hand, there are archaeological remains in the Metruk saltpan of the BTW. The Metruk saltpan is connected to the sea by 3 channels, with an extension of 7-m long, 2-m wide, and 1-m deep. The flow direction of the water in the connection channels between the Metruk saltpan and Bargylia Bay changes season to season. The road built



Figure 2. Hydrological properties and water budget components of the study area.

on the embankment from the Bargylia Bay separates the saltpan. Bargylia Bay is a small (272 ha), but relatively deep (>2 m), bay in Güllük Bay (Aegean Sea). In the past, sediments from Kocadere Creek were transported by small creeks to Bargylia Bay, and over time, sedimentation filled some parts of its little cove, making the Boğaziçi village coast shallow, like Metruk Tuzla (Altınsaçlı et al., 2015a).

The GCWS recharges from rainfall, as well as the Sarıçay and Mazı streams (samples 1, 2, 13, and 14), brackish karstic springs (samples 4, 5, 8, and 11) combined with the Sarıçay stream, irrigation channels (sample 6), waste waters of earthen pond facilities mixed with the Sarıçay stream (sample 9), and brackish groundwater (samples 3, 7, and 10) (Figure 2). Discharge of the GCWS occurs with evaporation, groundwater pumping, and irrigation channels. Changes in the system storage can be formulated as in the equation below:

 $\pm \Delta S = (P + R_1) - (E + ET + R_0) \pm Q_G \pm Q_1.$

Here, ΔS is the change in system storage per unit time, P is the areal total precipitation occurring on the system, R₁ is the total amount of water entering the system v is surface flow, E is the total evaporation occurring on the free water surface, ET is the total evapotranspiration occurring in swamp and marsh areas, R_0 is the total amount of water discharging from the system via surface flow, Q_G is the discharge and/or recharge to the groundwater system, and Q_1 is the incoming or exiting groundwater in the wetland system through drainage channels. The calculation could not be made due to lack of data.

According to Somay (2017), the average annual precipitation in Milas between 1950 and 2014 was 811.3 mm. In the same time interval, the annual average temperature was measured as 15 °C. In the calculation made by Somay (2017), using the method of Thornthwaite (1948), the corrected potential evapotranspiration value was found to be 824.5 mm. From January to March, the water surplus feeds the surface and the groundwater. The water deficiency, occurring in April, May, and June, is covered by the soil moisture reserve. However, agricultural water deficiency occurs between June and October.

Especially in this dry season, the amount of salinization increases due to both a lack of water surplus and a high value of evaporation at the same time. The soil moisture reserve is recharged with increasing precipitation again in November and December.

3. Material and methods

A total of 15 water samples were collected from the study area in April 2016. The samples consisted of surface water, 8 of which were from rivers and lagoons, 4 were from springs, and 3 were from ground water from drilling wells (Figure 1). Temperature, electrical conductivity (EC), and pH measurements of all of the water samples were performed using an on-site WTW multimeter (Xylem Analytics Germany Sales GmbH, Weilheim, Germany). The pH and EC measurements were accurate within ± 0.0005 units and $\pm 0.5\%$, respectively. The samples were collected in 50-mL polyethylene plastic bottles and filtered with 0.45-L filter paper. For the conservation of major cations (Ca, K, Mg, and Na) and heavy metals, 1 filtered (0.45 mm) sample was acidified with 1% HNO, to a pH of <2.4, which remained dissolved in the water sample. Another sample was kept unacidified for Cl, SO4, and HCO, analyses. All of the samples were stored at 4°C until they were analyzed.

Analyses were conducted by the accredited Actlabs Laboratory (Activation Laboratories Ltd., Ancaster, Ontario, Canada). The δ^{18} O and δ D isotope analyses were performed at the University of California Davis Stable Isotope Laboratory (Davis, CA, USA) using a Micromass-GVI Optima isotope mass spectrometer (Cheadle Hulme, UK). Vienna standard average ocean water was used as a standard and the measurement sensitivity for this standard was specified as 0.25‰ for $\delta^{18}O$ and 3‰ for δD (Somay, 2017). The current long-term meteorological data were collected from the Turkish State Meteorological Service website. The PhreeqCi (Parkhust and Appelo, 1999) software program was used to calculate the chemical equilibrium model of the waters to perform a wide variety of aqueous geochemical calculations based on an ion-association aqueous model. Canadian water quality guidelines for the protection of aquatic life (CWQG, 2014) standard and Turkish drinking water standards (TSE266;1997, 2005,2014)² were used to make a comparison with the data from this study.

4. Geological settings and hydrogeology

There are 3 stratigraphic sequences defined in the region (Figure 3). These are from the bottom to the top: Menderes Massif rocks, Lycian nappes rocks settled as allochthonous, and Neogene aged sediments covering these 2 rock groups. The upper part of the Menderes Massif cover sequence is represented by the Milas, Kızılağaç, and Kazıklı formations

² http://www.ccme.ca/assets/pdf/wqg_aql_ summary_table.pdf

(tectonic mélange). According to Rimmele et al. (2003), this cover sequence consists of Paleozoic schist overlain by Mesozoic to Cenozoic marble units. The Cenomanian-Campanian-aged Milas Formation is represented by sanded and fossiliferous, thick-layered platform type marbles. The Milas Formation, which spreads over a large area in the study area and is compatible with schists, consists of dolomitized limestone (Eroskay et al., 1992). The Milas Formation spreadst hrough Savranköy in the east of the study area, and is limited by the Kızılağaç, Karaova, and Kazıklı formations in the south. This formation is the major aguifer in the study area with a thickness of 1000 m (Figure 4). It is generally permeable and highly karstic. Karst springs discharge from impermeable schist contacts at the base of the formation (Barut et al., 2001). According to Önhon and Nazik (1998), the transmissibility of this unit was calculated as between 200 and 5275 m²/ day. High transmissibility values are generally seen in places where efficient fracture systems, in other words, karstification, are high in the study area. Hydrological and hydrogeological basin boundaries do not overlap in areas where karstic limestone is dispersed (Eroskay et al., 1992). Most of the Milas limestone is recharged from Paşalıdağ in the southwest. For example, some groundwater flow direction is from east to west. This means the discharge of the Milas Formation is generally towards Savranköy in the study area. On the other hand, in the same unit where groundwater flows to the southwest, there is a confined aquifer under Neogene cover rocks, which discharges as Ekinambarı Spring in the study area. The Late Campanian-Maastrichtian-aged (Arslan et al., 2013) Kızılağaç Formation is occasionally cherished pelagic marbles and metaconglomerates. Limestone levels below the formation have karstic structures and are permeable (Eroskay et al., 1992). Shale, marl, and silt levels at the upper levels of the formation are impermeable. Therefore, this formation is defined as a semipermeable unit due to the silty levels. The Middle Paleocene-aged Kazıklı Formation has flysch-type mélange rocks (Özer, 2012). The mélange, which mixes with the ophiolite, forms an impermeable barrier.

The allochthonous Lycian nappe complex that overlies the autochthonous Menderes Massif, consists, from base to top, of meta-sediments, a mélange unit, and an ophiolitic sequence (Rimmele et al., 2003). The Late Permian-Early Triassic-aged (Çağlayan, 1980) Karaova Formation, which is formed at the bottom of the Lycian nappes, consists of conglomerate, sandstone-shale layers, and limestone lenses of different sizes. The thickness of the formation is about 1000 m (Eroskay et al., 1992). This formation can be defined as impermeable, especially towards the Lycian Nappes. However, the lower part of the limestone levels have karstic features. When the discharge point of Ekinambari Spring is taken into consideration, it was



Figure 3. Geological map of the study area [from Arslan et al. (2013), Rimmele et al. (2003), and Hanilçi (2019)].

argued by Eroskay et al. (1992) that it relates to the Milas limestone. The Karaova Formation is tectonically overlain by the massive andthickly-bedded grey shallow-water dolomitic limestones of the Middle Triassic to the Middle Liassic-aged Gereme Formation (Arslan et al. 2013). The thickness of the formation was given as 600-750 m by Eroskay et al. (1992). The Gereme Formation is followed upwards bycherty limestones of the Late Jurassic to Late Cretaceous-aged Bodrum Formation (Arslan et al., 2013). Allochthonous Lycian nappes have very effective and widespread karstic features were having been affected by epirogenic movements. The average transmissibility of this unit was calculated as 395 m²/day (Önhon and Nazik, 1998).In this unit, because of the effective fracture systems, which are highly karstic, different transmissibility values were determined.

Lycian nappes, as well as their tectonic contacts, are unconformably overlain by coal-bearing Early Middle Miocene sedimentary successions (Yılmaz et al., 2000; Gürer and Yılmaz, 2002; Arslan et al., 2013). The Turgut Formation consists of shale, marl, and several lignite beds. The top of the sequence is a white marl and limestone unit called the Sekköy Formation (Atalay, 1980). The lacustrine limestone is overlain unconformably by a 100- to 200-m-thick conglomerate and sandstone unit known as the Yatağan Formation (Gürer and Yılmaz, 2002). Neogene sedimentary units can be defined as semipermeable units. Groundwater is drawn from the sandstone, limestone, and conglomerate levels of the Yatağan Formation via drilling. According to Ünal (2018), the permeability and transmissibility values of Yatağan Formation were calculated using the Cooper-Jacop method as 1.56×10⁻³-



Figure 4. Hydrogeological properties of the units [stratigraphic columns were taken from Arslan et al. (2013) and Gürer and Yılmaz (2002)].

 4.31×10^{-7} m/s and $1.39 \times 10^{0} - 8.6 \times 10^{-5}$ m²/s, respectively. It was seen that the permeability value decreased with thicker claystone, marl, and shale. The limestone levels of the Yatağan Formation have relatively high permeability, at 1.56×10^{-3} m/s.

Quaternary alluvium covers all the units with unconformity and consists of silt, clay, sand, and metamorphic pebbles. Although the clay- and siltdominant areas are impermeable, alluvium generally acts as aquifer in the study area. Since the effect of the precipitation factor in the structural distribution of the alluviums is very large, the transmissibility of the alluviums varies between 130 and 5500 m²/day (Önhon and Nazik, 1998).

5. Results

5.1. Hydrogeochemical evolution

Groundwater chemistry is mainly related to the mineral chemistry of the aquifer along the flow direction. The hydrochemical processes and hydrogeochemistry of groundwater vary spatially and temporarily, depending on the geology and chemical properties of the aquifer. However, the effect of seawater in coastal areas may change these processes. The hydrochemistry of such lagoons is clearly far from steady-state and their associated ecosystems generally exist in a precarious state (Kjerfve et al., 1996).

The dissolution of carbonate rocks in karstic areas is as follows:

Primarily, CO_2 in the atmosphere passes into the water via precipitation. Physically dissolved CO_2 becomes about 0.75% hydrated at 4 °C and forms carbonic acid (H_2CO_3). The H_2CO_3 , which exhibits strong acid property, is completely broken down by primary oxidation. Secondary oxidation is observed when the HCO₂-ion breaks down to form CO_3^{2-} and H⁺. As a physical process, when water and carbonate rock come into contact, ions result in a crystal structure. The newly formed CO_3^{2-} combines with the released H⁺ in step 3 and HCO₃⁻is formed. The solution on the contact surface becomes poor in terms of CO_3^{2-} . Therefore, the balance between the carbonate rock and the solution is disturbed and the dissolution continues. Several hydrogeological studies (Bayari and Kurttaş, 2002;Elhatip, 2003, Yüce, 2005; Ekmekçi et al., 2008; Ozyurt and Bayari, 2008; Bayari et al., 2011; Hatipoglu-Bagci, 2014;Gemici et al., 2016; Mansour et al., 2017) have been conducted in the karstic and submarine areas of the Aegean and the Mediterranean Sea coasts of Turkey.

A total of 15 water samples from springs, drilling wells, streams, and lakes were analyzed to evaluate the hydrogeochemical characters of the GCWS, salinity dynamics of the lagoons, and seawater effects on the coastal aquifers. The deficiency of the seawater samples was eliminated using the sample of Somay et al. (2008). The results are shown in Table 1. Generally, the water samples had pH values between 7.27 and 9.15 (neutral to slightly alkaline and alkaline) with +/- 0.49 standard deviation (SD). In general, the stagnant surface waters were alkaline in nature with pH values ranging between from 8.0 and 9.00. The samples that were taken from the lakes and

Table 1. Chemical analyses of the waters (SuW: surface water, GW: groundwater, SPR: spring, SW: seawater; nm: not measured *Somay et al. (2008), **Somay (2017).

No.	Sample location	Temperature (°C)	рН	EC (µS/cm)	S (‰)	Na+ (mg/L)	K+ (mg/L)	Ca ⁺⁺ (mg/L)	Mg++ (mg/L)	Cl ⁻ (mg/L)	HCO3- (mg/L)	SO4= (mg/L)	Water type (IAH, 1979)	Error (%)	δD** (‰)	δ ¹⁸ O** (‰)
1	SuW	12.7	8.07	276	0	18	3	34	6	15	122	24	Ca-Na-HCO ₃	2.8	-28.7	-5.47
2	SuW	16.6	9.15	450	0	18	4	54	11	46	100	57	Ca-Mg- HCO ₃ -Cl-SO ₄	4.7	nm	nm
3	GW	20.1	7.42	14500	8.4	3390	90	247	256	6600	354	668	Na-Cl	-5.8	nm	nm
4	SPR	20.1	7.41	18830	11.2	3540	110	257	293	6900	330	764	Na-Cl	-5.6	-20.5	-4.31
5	SPR	20.0	7.60	19240	11.5	4270	126	287	343	8100	307	927	Na-Cl	-4.6	-19.8	-4.13
6	SuW	21.2	7.92	17250	10.2	3250	105	267	287	6450	234	804	Na-Cl	-5.8	-21.7	-4.33
7	GW	21.1	7.35	7190	4.0	1292	40	133	118	2700	393	299	Na-Cl	-6.1	-24.0	-4.88
8	SPR	26.2	8.18	7480	4.1	1401	43	158	134	2750	225	504	Na-Cl	-6.2	-14.5	-2.63
9	SuW	20.8	7.86	23100	13.9	5480	123	232	351	9500	261	1089	Na-Cl	-2.3	nm	nm
10	GW	19.2	7.27	5080	2.7	811	23	176	103	1650	390	252	Na-Cl	-4.6	-29.1	-6.00
11	SPR	17.3	7.60	13860	8.0	3070	102	231	273	6100	249	682	Na-Cl	-5.8	-22.6	-4.60
12	SuW	21.2	8.19	15330	8.9	3870	87	232	248	6750	195	765	Na-Cl	-1.8	-21.8	-4.37
13	SuW	18.2	7.88	4030	2.0	782	17	226	61	1500	232	194	Na-Ca-Cl	4.9	nm	nm
14	SuW	16.5	7.80	799	0.1	47	4	97	23	71	298	96	Ca-Na-Mg- HCO ₃ -Cl-SO ₄	0.1	-23.9	-4.24
15	SuW	17.2	8.34	41000	26.0	11450	337	435	920	19600	110	1933	Na-Cl	0.9	2.1	0.50
SW*		17.2	8.28	58800	38.8	12720	399	413	1381	21702	156	2379	Na-Cl	2.5	*8.4	*1.61

stagnant parts of the river showed alkaline features. The EC values ranged between 276 and 41,000 μ S/cm. This large difference was related to the presence of waters with very different salinity in the GCWS basin. Under normal conditions, the amount of evaporation in lagoon systems with freshwater input is observed in dry seasons. However, according to both Alataş (1989) and Eroskay et al.(1992), salinity level changes in brackish karstic springs are not related to the season. These studies showed that the long-term EC values did not change in the Savranköy, İçmeköy, and Ekinambarısprings.

While tides are formed in lagoons, changes and fluctuations in the water flow can be easily transferred into the lagoon. In addition, in thesetypes of lagoons, salinity shows homogeneity and varies between 1‰ and 35‰, depending on freshwater inlet (Kjerfve et al., 1996). Brackish waters are found in the karstic areas up to several hundred meters from the seashore. According to the brackish and saline water classification of Beadle (1958), samples 1, 2, and 14 were freshwater with zero salinity (‰). Samples 7, 8, 10, and 13 were oligohaline water with salinity between 0.5‰ and 5‰. The İçmeköy drill well, İçmeköy, Ekinambarı, and Savranköy karstic springs, the stream in Avşar Village, Sarıçay Stream near the aquaculture pond, and Limni Lake were mesohaline water with salinity between 5‰ and 18‰. Only the intertidal bay, in the BTW, was polyhaline water with high salinity, at 26‰. The saltpan salinity was measured as 54‰ by Altınsaçlı (2015b). This datashowedt hat waters from the BTW were not only polyhaline, but also hyperhaline.

The ranges of Na⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻and SO₄²⁻ions were wide, comprising 18–11,450, 34–435, 6–920, 15–19,600, 110–393, and 24–1933 mg/L, respectively (Table 1). These wide distributions of the major ions showed that there is a saltwater effect in the wetland area. All of the

Table 2. Correlation matrix of the major ion of the waters.

major ions, except HCO₃, were very well associated with Cl (r^2 largert han 0.90), suggesting that they were likely derived from the saltwater source (seawater) (Table 2).To establish this, the relationship between Na and Cl is shown in detail in Figure 5 (Na-Clline 1:1),wherein the samples taken in the study area can be said to have weathering by ion exchange and/or the seawater intrusion process, since the line 1\1 plots into the Cl area.

According to Somay et al. (2008), the local seawater exhibits the typical chemistry (Na>Mg>Ca>K and Cl>SO₄>HCO₂) of the Aegean Sea in the close vicinity of the study area. When the relationship between SO4 and HCO3 was examined (Figure 6), it was seen that the Tuzla saltpan, Savranköy Spring, Limni Lake, Ekinambarı Spring, İçmeköy Spring, Yaykın Spring, and İçmeköy drill well were directly affected by seawater. In addition, the Mg/Ca ratio can be used to identify the seawater intrusion. According to Metcalf and Eddy (2000), the fact that the Mg/Ca ratio was more than 5 indicated direct seawater intrusion. The Mg/Ca vs. Cl diagram (Figure 7) shows that the sample waters with a Mg/Ca value greater than 1 are in the ion exchange and/or sea water intrusion process, except samples 1, 2, 10, 13, and 14. The dominant ions in the fresh groundwater are usually Ca, Mg, and HCO,, which are formed by the dissolution of calcite and dolomite. However, in the study area, all of the sampled groundwater samples were Na-Cl water, according to the International Association of Hydrogeologists (IAH) (1979) classification (Table 1).

Salinization and a change in the chemical composition of the groundwater is a result of natural or man-made factors that occur on the current path from the feeding area to the discharge area (Richter et al., 1993). The chemical composition of groundwater in a coastal aquifer is a function of the ratio of fresh/saltwater mixing from

	Temperature (°C)	pН	EC	S	Na+	K+	Ca++	Mg++	Cl-	HCO3-	SO4=
Temperature (°C)	1.00										
pН	-0.19	1.00									
EC	0.20	-0.04	1.00								
S	0.17	-0.02	1.00	1.00							
Na+	0.13	0.04	0.98	0.99	1.00						
K+	0.08	0.04	0.98	0.98	0.99	1.00					
Ca++	0.27	-0.19	0.91	0.91	0.89	0.89	1.00				
Mg++	0.10	0.03	0.98	0.98	0.99	1.00	0.90	1.00			
Cl-	0.14	0.01	0.99	0.99	1.00	0.99	0.90	0.99	1.00		
HCO3-	0.39	-0.89	-0.12	-0.14	-0.20	-0.22	0.03	-0.20	-0.17	1.00	
SO4=	0.23	0.01	0.99	0.99	0.99	0.98	0.91	0.98	0.99	-0.16	1.00



Figure 5. Na and Cl relationship of the waters.



Figure 6. SO₄ and HCO₃ relationship of the waters.

different salinity sources, such as water–rock interaction, cation exchange, redox reaction, carbonate and evaporate mineral dissolution, old salty water tapped in the aquifer, and seawater/saltlake intrusion (Mirzavand et al., 2020).

Seawater mixing rates in the groundwater in the study area were calculated (Table 3). Chloride is generally used

in salinity studies. The reason for this is that although some ions undergo chemical changes in the current pathway, hydrogeochemical processes do not affect chloride. The chloride means of samples 1 and 2 in the basin provided the first end component (freshwater end component= 0.35 meq/L), and the seawater was the second end component



Figure 7. Mg/Ca vs. Cl relationship of the waters.

Sample	Names	Cl (meq/L)	Elevation (m)	Distance from the sea (km)	Mixing ratio (%)
1	Sarıçay Stream	0.42	25	16	0
2	Sarıçay Stream	1.30	24	14	0
3	İçmeköy well	186.03	20	12	30
4	İçmeköy Spring	194.48	23	11	32
5	Savranköy Spring	228.30	24	11	37
6	Avşarstream	181.80	7	9	30
7	Avşar well	76.10	9	7	12
8	Yaykın Spring	77.51	3	3	13
9	Sarıçay Stream (fishery farm)	267.76	1	1	44
10	Koruköy pump	46.51	11	8	8
11	Ekinambarı Spring	171.93	9	7	28
12	Lake Limni	190.25	1	0	31
13	Stream	42.28	14	1	7
14	Mazı Stream	2.00	1	1	0
15	Tuzla saltpan	552.44	0	0	90
SW	Seawater	611.32			100

Table 3. Seawater mixing ratios, in percentage, of the sampled waters.

(saltwater end component= 611.98meq/L). Seawater mixing ratios, in percentage, of other samples were found using the following equation (Kurttaş and Bayarı, 1999):

Contribution of the end component (mixing ratio)

$$=\frac{Cl_{sample} - Cl_{fresh water}}{Cl_{seawater} - Cl_{fresh water}} \times 100 \,(\%)$$

According to this equation, the following results (Table 3) were calculated:

It can be clearly seen that brackish karstic springs had much more seawater mixing than freshwater (Table 3). Savranköy was the most saline karstic spring in the area, with a seawater mixing ratio of 37%. The mixing ratio of İçmeköy Spring, Lake Limni, and Ekinambarı springs was about 30%. Yaykın Spring was the least affected by the seawater mixing, with higher fresh groundwater input than the other brackish karstic springs.Other surface waters that had a high mixing ratio were related not only to the evaporation process, but also the mixing of large amounts of brackish waters with them.

The total dissolved solid value and Na / (Na + Ca) ratios of the water samples were placed on the Gibbs diagram (1970) in order to determine the function and mechanism of the water samples from the study area. On the Gibbs diagram,3 different areas were defined, which indicated that evaporation/crystallization, and rock and precipitation dominance were effective in the development of the water types. According to the analysis results of the water samples in the study area, all of the water samples, except the 1, 2, and 14 freshwater streams, were in the evaporation/crystallization region (Figure 8). The waters in this region are salted due to seawater intrusion and are exposed to intense evaporation. Therefore, the total amount of dissolved ions in the water reaches high values. The evaporation/crystallization rate increases from both Avsar to Savranköy and Koruköy to İcmeköy, that is, from coast to inland. In addition to this, if a comparison is made within the springs, the Yaykın Spring is less salted than the other brackish karstic springs, even though it is closer to the sea. This shows that the freshwater input is higher in the Yaykın karstic spring.

The water samples taken from the study area were also interpreted in the Schoeller semilogarithmic diagram for origin research (Figure 9). The waters taken from the coastal areas had the same peaks when compared to those of the seawater. However, the stream waters coming from the upper part of the basin (samples 1, 2, and 14) had different peaks that the coastal section. This shows that the coastal and upper basin sections are of different origins. As shown in Figure 9, all of the groundwater samples have the same peak with the seawater, which indicates as eawater intrusion.

In this study, a Piper diagram (1944) was used to classify and define the hydrogeochemical functions of both the groundwater and surface water. Under normal conditions, limestones, dolomite, and marl produce Ca-Mg-HCO₃ water. However, in the study area, all of the spring waters and groundwaters plotted in the alkaline elements exceeded the alkaline elements, the strong acids exceeded the weak acids, and noncarbonate alkalinity exceeded 50% of the areas, except samples 1, 2, and 14 (Figure 10). These areas showed a seawater intrusion in the study area with Na-Cl water in the diagram.

The δ^{18} O and δ D contents of the samples were between -6.00%, and 0.50% and -29.1% and 2.1%, respectively(Somay, 2017). The waters in the study area were plotted between the global and Mediterranean meteoric water lines,



Figure 8. Gibbs diagram of the waters.

and on the saltwater mixing line (Figure 11). According to the study of Somay (2017), it is clearly seen that İçmeköy, Savranköy, and Ekinambarı springs were plotted on the dissolution salts-leaching trend (Figure 12). This trend explains the presence of paleo-karst groundwater and the dissolution of marine sediments in the area. Avşar Stream and Limni Lake were plotted between the dissolution salts and seawater mixing line due to the fact that high amounts of brackish water was added to these water bodies. The Avşar groundwater and Tuzla saltpan were plotted close to the seawater mixing line.

5.2. Heavy metal content, saturation, and species

The computer program PHREEQCi (Parkhust and Appelo 1999), using the llnl.dat,was used to calculate saturation index (SI) and aqueous species. The calculated SI benefits indicate whether the solution is undersaturated (SI < 0.5),



Figure 9.Schoeller semilog diagram of the waters.

at equilibrium (SI = 0), or oversaturated (SI > 0.5), with respect to the mineral under consideration (Plummer et al., 1988). In general, all of the samples were oversaturated with calcite, dolomite, kaolinite, K-feldspar, and quartz (SI > 0.5) (Table 4). Contrariwise, all of the water samples were undersaturated with gypsum, halite, and barite (freshwater samples) (SI < 0.5) (Figure 13).

In the study area, the heavy metal content of the water samples was interpreted based not only on the TSE266 (1997, 2005, 2014), but also on the CWQG (2014), due to the wetland features of the study area. According to Table 5, the Al, Cu, and Zn values exceeded the tolerance limit of the CWQG (2014) standards in some of the water samples. If these water samples were evaluated according to the TSE266 (1997, 2005,2014) drinking water standards, it seems that no water sample exceeded the tolerance limits. Bauxite ores (Figure 2) may probably be the main sources of relatively high concentrations of Al in samples 7, 8, 10, and 15. Relatively high Cu and Zn contents of some of the waters may have been related to the drilling pipes and agricultural pesticides that are used in the study area. Agricultural activities are widely conducted in Avşar. According to Dalman et al. (2006) and Balkıs et al. (2013), high Pb, Cd, and Zn concentrations in surface sediments indicate terrestrial and anthropogenic (domestic + industrial) inputs, especially coming from Sarıçay Stream to Güllük Bay, as the result of sea transportation in ports and tourism activities.

In addition, the presence of the feldspar grinding and flotation facilities in the area near the GLW adds an extra



Figure 10. Piper diagram of the waters.



Figure 11.δO¹⁸-δD diagram (modified from Somay, 2017).

feldspar mineral to Limni Lake. The byproducts of feldspar dissolution are mainly clay minerals (e.g., kaolinite and K-feldspar) and authigenic quartz (Emery et al. 1990). This will make the lake water, which is already oversaturated with kaolinite and K-feldspar, even more saturated (Table 4).

5.3. Irrigation water quality

In coastal areas, the waters used in irrigation contain a high number of dissolved ions, and these ions affect plants and soil, both physically and chemically, and decrease the yield. Na+ in saltwater replaces Ca²+ in the soil, and reduces permeability and aeration of the soil. In high salinity soil solution environments, plants will begin to turn yellow and lose their turgor, as if under drought. Semiarid countries like Turkey use rather salty water for irrigation.Pollution sources should be controlled, and the management of domestic sewage and industrial wastewater discharge, and agricultural fertilizer use,should be given importance for



Figure 12.6O¹⁸-Cl diagram (modified from Somay, 2017).

	Albite	Calcite	Dolomite	Gypsum	Halite	Barite	Quartz	K-Felds	Kaolinite
1	0.64	0.10	0.80	-2.45	-8.09	-0.66	0.46	2.93	4.96
2	-0.76	1.17	3.02	-1.97	-7.61	-0.25	0.03	1.53	1.50
3	1.36	0.35	2.11	-1.12	-3.41	0.03	0.12	2.66	4.31
4	1.19	0.31	2.08	-1.07	-3.38	-0.09	0.00	2.56	4.43
5	-	0.48	2.43	-1.00	-3.24	-0.08	-0.03	-	-
6	0.93	0.70	2.83	-1.01	-3.44	0.13	-0.03	2.30	3.02
7	2.07	0.22	1.78	-1.48	-4.04	-0.01	0.17	3.31	6.17
8	-	0.91	3.16	-1.20	-4.07	0.13	-	-	-
9	1.36	0.54	2.67	-1.07	-3.08	0.11	-0.14	2.57	4.04
10	1.92	0.30	1.74	-1.31	-4.54	0.36	0.28	3.26	6.29
11	1.19	0.31	2.08	-1.12	-3.48	-0.02	-0.02	2.64	4.37
12	1.44	0.80	3.04	-1.11	-3.35	0.08	-0.07	2.65	3.58
13	-	0.78	2.36	-1.29	-4.53	0.57	-	-	-
14	0.49	0.62	1.97	-1.60	-7.04	0.37	0.20	2.37	5.22
15	-	0.65	3.02	-0.84	-2.49	0.13	-	-	-

Table 4. Mineral saturation indices of the water samples.

the sustainable use of groundwater resources, especially in agricultural areas (Liu et al., 2019).

In addition to the water quality, plant development also effects the characteristics, such as soil type, permeability, climatic conditions, amount of water used, plant type, irrigation methods, and cultivation methods applied.

The amount of sodium plays an important role in irrigation water. Sodium, disrupts the structure of the soil, reduces permeability, and causes a crust on the soil after watering. In addition, sodium creates a toxic environment for plants (Zong et al., 2016; Haque and Matsubara, 2018; Hayat et al., 2020).

The plain around the GLCW is used for agricultural purposes. In addition to agricultural products, such as corn and wheat, citrus is also grown in the plains around the GLW. In addition, there are olive groves around the BTW. However, there is a salinization problem for these agricultural areas. One of the reasons for salinization in



Figure 13. Saturation index of some minerals in the water.

Samples	Al (µg/L)	As (µg/L)	Cu (µg/L)	Fe (µg/L)	Li (µg/L)	Mn (μg/L)	Pb (μg/L)	Si (µg/L)	Zn (µg/L)
1	34	9.1	3.2	62	5	30.7	1.0	8894	29.5
2	30	6.7	2.9	<10	4	11.2	1.5	4531	40.3
3	23	< 0.3	3.8	110	43	57.3	0.6	5900	38.0
4	34	<0.3	2.4	<100	55	7.3	0.5	4500	38.7
5	<20	< 0.3	2.6	<100	63	3.0	0.5	4200	23.4
6	24	< 0.3	3.7	<100	53	19.4	0.7	4600	68.7
7	160	1.2	54.0	<100	23	15.0	0.7	6900	266.0
8	120	1.8	25.0	260	29	210.0	1.0	<2000	112.0
9	88	1.0	4.3	<100	59	79.2	0.7	3500	43.1
10	120	<0.3	7.0	2890	16	39.0	1.3	8100	331.0
11	37	0.3	5.0	220	53	15.2	1.0	3800	60.7
12	88	0.4	8.5	<100	46	43.5	1.1	4400	50.2
13	68	1.0	7.0	<100	11	120.0	27.9	<2000	66.2
14	71	1.4	2.4	33	3	90.8	1.2	5929	227.8
15	230	<0.6	7.6	450	3180	51.0	0.8	<4000	55.8
TSE 266	200	10	2000	200	-	50	10	-	5000
CWQG	100	5	2-4	300	-	200	1-7	-	30

Table 5. Some trace and heavy metal contents of the water samples.

the soil in these regions is an insufficient amount of rain, whereas evaporation is high. According to Altınsaçlı (2013), it was determined that the soils in the region are very salty-sodic (8–12 mS/cm) and only soils that can yield normal yields from salinity-tolerant plants can be found in the study area.

The EC, magnesium hazard, sodium-excess and sodium adsorption ratio values were examined to determine whether the groundwater is suitable for agricultural purposes (Table 6).The formulas, classifications, and quality of waters are given in Table 6.According to the irrigation water quality assessment, the İçmeköy, Savranköy, Yaykın, and Ekinambarı springs, and streams in Avşar and those located near the aquaculture farm, Lake Limni, and the Tuzla salt pan are not suitable for irrigation proposes. They have harmful effects on plants due to their high concentration Na.

6. Discussion and conclusion

The GCWS (not only the GLW, but also the BTW), hosts many different industries, such as fisheries, aquaculture, airport facilities, tourism, port transportation, and agriculture. These industries provide great contributions to the Turkish economy. The GCWS was studied in terms of its hydrogeology and hydrogeochemistry. The investigation and determination of the hydrogeological properties of the waters will ensure that the groundwater resources are managed correctly.Plans for groundwater management are a basic method of managing groundwater. It is vital to ensure that they are robust and effective.

The fact that this wetland has both the karstic features and is in the lagoon system, means that it is vulnerable to many pollutants, such as seawater intrusion, wastewater from fishery factories, feldspar grinding-flotation facilities, and agricultural pesticides. Mixing of any of these pollutants into the wetland will have animmediate effect. The fact that karstic environments are anisotropic and heterogeneous in terms of groundwater flow causes great changes in terms of the quality, time, and location, as well as the amount, of groundwater. It is a known fact that coastal karstic aquifers are more vulnerable to seawater intrusion than other coastal aquifers. In addition to karstic features, lagoons are known as very sensitive habitats for hydrodynamic reasons. The salinization mechanisms of coastal confined and unconfined karstic aquifers are becoming more and more complicated with the geological time sea level changes and/or seawater intrusion, and the already salted tidal surface waters. The high-volume salt content of the ground and surface waters may have derived from direct recent or historical seawater intrusion, irrigation return canals, wastewaters of inland pond aquaculture farms, swamps, and marshes that recharge on seawater and salt flats-ponds in the GCWS.

Brackish karstic waters are slow-acting saline liquids that entered the aquifers in the previous transgression during the Quaternary period with seawater intrusion, as mentionedby previous researchers. According to Darkot and Erinç (1954), the highland sea with Flandrian transgression after Würm glaciation was filled with collapsed areas through the valleys. Hence, the Güllük, Milas (GLW), and Tuzla (BTW) plainswere located under seawater. The BTW is connected to GüllükBay through a strait formed by the abyss of an old valley deep under the sea. This process has changed the water-rock interaction in the karstic aquifers. Mixing with saltwater is caused by calcite dissolution and precipitation, and dedolomitization in the aquifer. According to the salinity values of the sampled waters, they can be classified as mixohaline water with values ranging between 0.1‰ and 26‰. The high seawater mixing ratio of the İçmeköy and Savranköy springs (between 32% and 37%), which are discharged within 11-12 km from the sea, is controlled by the

Parameters	Formula	Range	Classification	Samples
EC		<pre><250 250-750 750-2000 2000-3000 >3000</pre>	Excellent Good Permissible Doubtful Unsuitable	1, 2 14 3, 4, 5, 6, 7, 8, 9,10, 11,12, 13,15
МН	$MH = \frac{rMg}{rMg + rCa} * 100$	<50 >50	Suitable Unsuitable	1, 2, 10, 13, 14 3, 4, 5, 6, 7, 8, 9, 11, 12, 15
Na%	$Na \% = \frac{rNa + rK}{rNa + rK + rMg + rCa} * 100$	<20 20-40 40-60 60-80 >80	Excellent Good Permissible Doubtful Unsuitable	2 1, 14 6, 8, 10, 13 3, 4, 5, 7, 9,11, 12, 15
SAR	$SAR = \frac{rNa}{\sqrt{\frac{rCa + rMg}{2}}}$	<10 10-18 18-26 >26	Excellent Good Permissible Doubtful	1, 2, 14 10, 13 7, 8 3, 4, 5, 6, 9, 11, 12, 15

Table 6. Irrigation water quality parameters of the waters.

EC: Electrical conductivity, MH: magnesium hazard, Na%: sodium-excess, SAR: sodium adsorption ratio.



Figure 14. Hydrogeological conceptual model of the study area.

geological structure and previous transgression (Figure 14). Accordingly, the EC values of the waters offer a wide range of changes (between 276 and 41,000 µS/cm), due to the different recharge areas and different seawater mixing ratios. In this context, all of the water samples were Na-Cl water according to the IAH classification, except samples 1, 2, and 14 (Sarıçay and Mazı Streams). According to the relationship between the Na and Cl ions, weathering via ion exchange and/or the seawater intrusion process can be clearly determined. Considering the mineral saturation status of the waters, it was seen that all of the samples were oversaturated with calcite, dolomite, kaolinite, K-feldspar, and quartz (SI > 0.5). According to the heavy metal content of the waters, the Al, Cu and Zn values exceed the tolerance limit of the Aquatic Life standards in some of the water samples. Finally, if the waters were evaluated for irrigation water purposefully, it would be clearly seen that the İçmeköy, Savranköy, Yaykın, and Ekinambarı springs, and streams in Avşar and those located near the

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Consequently, The GCWS is a unique wetland system that occurs in a brackish karstic formation, and sensitive and productive lagoon. Not only ecological and hydrological studies, but also hydrogeological and hydrogeochemical studies, should be conducted regularly to ensure groundwater sustainability and control elements that can damage and pollute the wetland.

Acknowledgments

The author would like to thank anonymous referees who made valuable comments and suggestions concerning our manuscript and the editors of Turkish Journal of Earth Sciences for their valuable comments and suggestions to improve the quality of the paper. Thanks are also given to Ulvi İbrahim Soyuçok, Sibel Çakır, and Okan Barbaros for their valuable help in the field study. Çağrı Altaş is thanked for proofreading of the paper.

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