## HYDROGEOLOGY AND HYDROCHEMISTRY OF MARBLE AQUIFER WITH POINT RECHARGE FROM TWO DEEP SINKHOLES, MENDERES MASSIVE, WESTERN TURKEY

# HIDROGEOLOGIJA IN HIDROKEMIJA MARMORNEGA VODONOSNIKA S PONORNIM TOČKOVNIM NAPAJANJEM (MASIV MENDERES, ZAHODNA TURČIJA)

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#### Abstract

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Celalettin ŞimŞek, Birol Kaya, Ahmet Alkan, Fatih Büyüktopçu, Necdet Türk & Yalçın Arisoy: Hydrology and hydrochemistry of marble aquifer with point recharge from two deep sinkholes, Menderes Massive, western Turkey

Menderes Massive is a NE-SW-trending metamorphic terrain in western Anatolia. The massive is composed of regionally metamorphosed rocks of mica-schist and marble. The Bozdag Mountain is the main horst system in Kucuk Menderes river basin. It is composed of several N-S oriented small horsts and grabens and contains important karst features, such as poljes and sinkholes. Ayvacik and Subatan Poljes are typical closed depressions draining into Ayvacik and Subatan sinkholes (ponors). Both are developed along the N-S directed fault system. The main objective of this study is to determine the karstification and hydrogeochemical features of water circulating in marble terrain and controlled by deep sinkholes in the Bozdag Mountain. Detailed speleological studies demonstrated that the degree of karstification of marble rock depends on the regional tectonic structure, the mineralogy of marble and the water recharge rate into the sinkholes. Tritium isotope and tracer tests indicate very fast flow and connection between Subatan surface water and a spring in lower elevations with high Ca and Mg ion concentration at the south of the study area.

**Keywords:** Marble rock, karstification, sinkholes, Bozdag Mountain, Menderes Massive, Western Turkey.

Izvleček

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Celalettin ŞimŞek, Birol Kaya, Ahmet Alkan, Fatih Büyüktopçu, Necdet Türk & Yalçın Arisoy: Hidrogeologija in hidrokemija marmornega vodonosnika s ponornim točkovnim napajanjem (Masiv Meredes, zahodna Turčija)

Masiv Menderes je območje metamorfnih kamnin v zahodni Anatoliji, Turčija. Razteza se v smeri SV-JZ in je sestavljeno predvsem iz regionalno metamorfiziranih sljudnih skrilavcev in marmorjev. Goro Bozdag sestavlja sistem manjših grud in tektonskih jarkov, orientiranih v smeri sever-jug. Masiv je delno zakrasel, s tipičnimi kraškimi oblikami, med katere spadata tudi polji Ayvacik in Subatan, ki se drenirata skozi istoimenske ponore. Obe polji sta razviti v prelomni coni orientirani v smeri sever-jug. Glavni namen opisane raziskave je določiti stopnjo zakraselosti območja in hidrokemične lastnosti vode, ki teče skozi marmornati masiv. Podrobne speleološke raziskave so pokazale, da je zakraselost močno pogojena z regionalno geološko strukturo, mineraloško sestavo marmorja in velikostjo dotokov v ponore. Izotopske analize tritija in sledenje podzemnih voda kažejo na hiter tok in povezavo med poljem Subatan in visoko mineraliziranimi izviri na jugu obravnavanega območja.

Ključne besede: Marmor, zakrasevanje, ponor, gora Bozdag, masiv Menderes, zahodna Turčija.

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## INTRODUCTION

In Turkey, carbonate formations are predominantly encountered in the Aegean region and along the Mediterranean coastline within the Taurus Mountain range. Generally in the Aegean region and particularly around Izmir, the karstic formations are classified as allochthonous limestone in flysh units and massive marble rock in the Menderes Massive (Fig. 1). The massive carbonate rocks are generally characterized by their well-defined stratigraphy and large spatial extent, whereas allochthonous limestone formations are typically distinguished with their deformed geology and limited spatial extent (Erdogan & Gungor 1992; Simsek *et al.* 2008).

Carbonate formations are generally marbles found as metamorphic rocks within the Paleozoic Menderes

Massive. The thickness of marble layers are variable but could reach up to 300 m (Erdogan & Gungor 1992). Marble mainly consists of dolomite minerals and is tectonically highly fractured (Yavuz *et al.* 2011). Karstic features such as sinkholes and caves are developed within the marble rock unit. The marble also host a number of large springs with discharges exceeding 200 L/s. Karstic water is used as drinking water resource in Odemis town and its vicinity in the south of Izmir Province (Fig. 1). This study is intended to characterize the karstification and hydrogeochemical features of karst groundwater occurring in the marble units of the Bozdag Mountain of the Menderes Massive in Izmir Province.



## DESCRIPTION OF THE STUDY AREA

The study area is located within the boundaries of Izmir Province in western Turkey. It is situated approximately 150 km south of the city of Izmir (Fig. 1). Bozdag Mountain is the highest mountain in the region that is famous for its ski center in western Turkey. Paleozoic aged marble rocks are found in the upper parts of the Bozdag Mountain. There are several small plains in the Bozdag Mountain region which are mostly used for agriculture. The mountainous fields are not suitable for settlement because of their high altitudes. The town of Odemis is the main population center in the area located in the southern outskirts of the Bozdag Mountain. The marble aquifer in the study area is a potential water resource for supplying the water demand of this town.

#### GEOLOGICAL SETTING

The study area is located in the Alpine-Himalayan orogenic belt, and is a part of tectonically active zone with numerous fault lines (Sozbilir 2002). The major tectonic lines observed in the study area are the E–W directed graben faults with lengths ranging up to 100 km, which are cut by N–S directed secondary faults (Inci 1991; Suzen *et al.* 2006). Major E–S running graben system is the Kucuk Menderes Plain surrounded by Bozdag Mountain to the north, which is the main horst system in the area. The N–S running secondary fault system controls the karst features developed in the Ayvacik and Subatan poljes (Fig. 2).







Fig. 3: Geological block diagram of the study area (Simsek et al. 2010).

Paleozoic aged Menderes metamorphic rocks form the basement of the study area and outcrop in many parts of the Bozdag Mountain (Simsek et al. 2010; Kaya et al. 2012) in western Turkey (Fig. 2). The Menderes metamorphic rocks consist of mica, calc-schist and massive marble in their upper level (Hetzel et al. 1998). Marble rock in the Menderes Massive is divided into three parts as low, middle and upper levels. The lower level of marble unit is represented by bedded marble layers that include thin lenses of mica schist. The middle part of the marble layer contains 50-60 m thick marble lenses sequenced with calc-schist. The upper part of the marble unit is characterized by emery bearing marbles that are widely observed in western of the Kucuk Menderes Basin (Erdogan & Gungor 1992; Gungor & Erdogan 2002; Yavuz et al. 2011). In the study area, the NS-SW trending upper part of the marble in the massive was observed with grey color and a total of thickness of 100 m as shown in Fig. 2. The Quaternary alluvial deposits overlie the Menderes Massive rocks in N-S running graben system.

#### HYDROGEOLOGICAL SETTING

The study area has the typical Central Aegean climate characterized by hot and dry summers, and cold and rainy winters. In addition, Ayvacik and Subatan poljes also receive snow in the winter (Fig. 3). These poljes are closed depressions collecting surface waters from the nearby terrain that later drain into the Ayvacik and Subatan sinkholes. The surface areas of Subatan and Ayvacik Poljes are 2.8 km<sup>2</sup> and 12.24 km<sup>2</sup>, respectively. The flow rate measurements in the area were made during the wet season of 2010. The flow rate of Ayvacik stream that drains the Ayvacik Polje in February was 21 L/s. The flow rate then decreased in March (2.8 L/s) and April (1.2 L/s). The Subatan polje is drained by two streams in the north and south of the plain, which confluence near Subatan sinkhole (Fig. 3). The total flow of these streams was 366 L/s, 196 L/s, and 94 L/s in February, March, and April, respectively. During the summer months, both Ayvacik and Subatan surface waters are dry, but limited flow was observed in the base of sinkholes. Camyayla (SP5 and SP8), Pitrak (SP6) and Su cikti (SP7) are the main springs located on the south and west of the study area (Fig. 2). The hydrogeology of the study area is governed by two major aquifer systems (Fig. 2). The first one is the unconfined alluvial aquifer that provides the majority of groundwater for irrigation in the Ayvacik and Subatan plains. The alluvial aquifer is mainly composed of sedimentary sand and gravel deposit that reach up to 90 m in thickness. The second aquifer, on the other hand, is the marble aquifer controlled N-S oriented fault lines (Figs. 2 and 3).

## MATERIALS AND METHODS

Two-stage investigation has been carried out in this study: (i) field and speleological study and, (ii) hydrochemical, isotope and tracer analysis. The field and speleological studies were carried out to determine the groundwater flow mechanism in the marble unit. The groundwater sampling and tracer analyses were performed to determine the water characteristic and marble hydrogeology. The water samples collected from eight sampling points were analyzed for major anions, cations and potential pollutants. The 50 mL sample collected from each point was first acidified in the field by nitric acid to drop the pH level below 2. This prepared sample was then analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for major cations and several trace elements, such as aluminum, arsenic and iron in Canadian ACME Laboratories. The 500 mL water sample collected from each sampling point was used for major anions analysis such as chloride, nitrate, sulfate, and bicarbonate ions. The bicarbonate analysis was performed by titrimetric techniques, whereas the remaining anions were analyzed by ion chromatography (IC) in the Dokuz Eylul University laboratories. Finally, the 1000 mL water samples collected from five selected springs and surface waters were tested for  $\delta^3$ H (tritium) in the isotope laboratories of Hacettepe University, Turkey. A tracer test was conducted with 1 kg of Uranine by injecting into the Subatan sinkhole and monitoring from Camyayla and Pıtrak springs.

### **RESULTS AND DISCUSSION**

#### KARSTIFICATION OF MARBLES

Structural mapping and speleological studies were conducted in sinkholes in Bozdag marble area to determine the marble aquifer karstification features. Joint systems are important pathways of ground water flow. The layers and faults are found to be concentrated at 174/24 and 260/35 directions in the marble unit. The discontinuity aperture was found to vary between 1-50 mm in the surface. The dips of the main discontinuities are near vertical and generally run in N-S directions. The main fault system is N-S directed and controls several small horst and graben systems in the area and separates several marble blocks from one another in the study area. Ayvacik, Subatan and Camyayla poljes were developed along the main N-S directed fault system in the Bozdag Mountain region as shown in Fig. 2 and 3. The main karst features of the study area are Ayvacik and Subatan sinkholes developed along the N-S directed small graben faults. All surface waters within enclosed poljes drain into the marble unit through these sinkholes.

Based on the speleological survey, the length and depth of the Ayvacik sinkhole were found to be 1575 m and 239 m, respectively. The Ayvacik sinkhole descends in a spiral form along the vertical fault zone as show in Fig. 4. Ayvacik sinkhole can be divided into three main morphological structures. The first section starts from the surface to the depth of 100 m with a vertical slope that consists big shafts and caves with very dense small fracture system in the massive marble unit (Fig. 4). The second morphological feature continues from to 100 m down to the depth of 200 m at a slope angle of 20°. The second section has very complex morphological features like labyrinths that include enlarged fracture zones and narrow passages. In addition, there is a big hall in this section, whose height varies between 25 m to 30 m and total area is approximately 1500 m<sup>2</sup>. This hall consists of mainly marble with intercalations of medium to small

thick mica-schist layers. The third morphological unit consists of very small fracture zones and a narrow shaft with a mild slope ending at the depth of 239 m with a siphon. It consists of marble units including very thick mica and calc-schist layers. Similarly, the Subatan sinkhole occurs along the N–S running faults within the Subatan polje. Total depth of Subatan sinkhole is 150 m (Fig. 5). Subatan sinkhole developed through the marble and schist contact zone controlled by the graben fault and ends at a similar siphon feature. These results indicate that Subatan and Ayvacik sinkholes end at the bottom of the marble layer, creating bottom siphons. These siphons are also filled with sediments including sands, clays and silts as well as organic material coming from the surface agricultural lands.

### HYDROCHEMICAL CHARACTERISTIC

The results of chemical analysis of the water samples collected from surface waters (SP1, SP2 and SP3) and some important karst springs (SP4, SP5, SP6, and SP7) in the study area (Fig. 2) are presented in Tab. 1. The range of pH values for all samples is between 7.11 and 7.96, indicating neutral to weak alkaline waters. The temperature values range from 11.2 to 14.5 °C. The electrical conductivity value varies from 281 to 373 µS/cm. The physical characteristics of these waters show slightly alkaline and low mineral content as seen Tab. 1. Water chemistry of the marble aquifer are dominantly Ca-HCO<sub>3</sub>. The surface water samples were found to differ from the spring waters; while Na and K were predominant elements in the surface waters, Ca and Mg were the major ions in the spring waters. Since marble is dolomitic, the dissolution of dolomite increased the Ca and Mg ions in the spring waters.

Na was found to be at concentrations between 4.24 to 12.72 mg/L. The highest Na value was observed in the surface water and a high level K concentration was also



Fig. 4: Cave map of the Ayvacik sinkhole (Simsek et al. 2010).



obtained in the surface water (Tab. 1).  $SO_4$  concentration ranged from 2.99 to 47.93 mg/L, with highest value observed in S6 sampling point. The nitrate concentrations in the surface and spring waters were between 0.1 and 25.3 mg/L. The highest nitrate concentration was found in the surface water and the spring water at sampling point of SP2. It is known that main nitrate sources in groundwater are mineral deposits, soils, agricultural fertilizers, biota and sewage (Evangelou 1998). Since nitrogenous materials are rare in the geological materials, presence of nitrate in the groundwater is due to anthropogenic activity. Therefore, some fertilizers from the agricultural activities play very important role in deteriorating the surface water quality in the Ayvacik and Subatan enclosed poljes.

Chemical analysis results of the water are shown on a Schoeller's semi-logarithmic diagram in Fig. 6. From the Schoeller's semi logarithmic diagram, it is clear that the surface water samples taken from SP1, SP2 and SP3 locations have similar chemical characteristics (Fig. 6).

Fig.5: Cave map of the Subatan sinkhole (Simsek et al. 2010).

Table 1. Chemical results of the sampling points

		×	٢	Z	Ηd	EC	Eh	Т	NO <sub>3</sub> -N	Na	х	Ca	Мg	מ	нсо <sub>3</sub>	SO₄	AI	As	Fe	ИN	TU
Samplin	g No					μS/cm	тV	°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	%
	SP1	585273	4245261	1015	7.3	281	0.264	11.5	0.1	11.38	1.34	34.6	12	13.0	147.6	44.94	0.029	0.0005	0.017	0.004	6.62
	SP2	585602	4245823	962	7.96	305	0.26	14.8	11.3	7.75	1.42	59.8	5.5	9.0	139.1	11.98	0.01	0.0015	0.01	0.031	6.69
Surface Waters	SP3	585602	4245823	962	7.58	327	0.279	13.9	25.3	12.72	2.45	41.6	14	13.0	73.2	47.93	0.01	0.0007	0.011	0.015	
	SP4	580559	4245014	970	7.45	356	0.21	11.8	9.4	5.31	0.72	79.7	4.8	8.0	187.9	8.98	0.002	0.0005	0.01	0.00	
	SP5	582068	4247278	860	7.39	334	0.289	13.1	6.8	6.64	0.65	66	6.9	7.0	185.4	5.99	0.003	0.0015	0.01	0 <sup>a</sup> °.00	5.95
	SP6	582270	4243188	625	7.35	350	0.21	12.9	14.6	10.11	1.68	60.2	11	10.0	144	29.96	0.058	0.0014	0.066	0.008	5.31
Spring	SP7	580687	4241908	730	7.53	373	0.227	12.9	1.5	4.24	0.43	86.2	8.7	6.0	222	14.98	0.008	0.0005	0.01	0.0001	
Waters	SP8	582524	4247154	880	7.11	333	0.282	14.2	N.A.	8.29	0.87	61.9	11	5.0	235.5	2.99	0.007	0.0003	0.01	0.002	5.28
	(WHO 2004)								10								0.2	0.01	0.2	0.4	



Fig. 6: Semi-logarithmic schoeller diagram of the waters.

The results of elemental analysis covered toxic and trace elements found in surface and spring waters are shown in Tab. 1. Especially, Al and As are found to be well beyond the typical values that would normally be found in cold waters (WHO 2004). The surface waters generally effected by agricultural activity and some toxic fertilizer contaminates the surface waters. The highest Al value was found in the SP6 spring water that emerged from fault system in the south of the study area. Al and As in SP6 is mainly derived from the agricultural activity, including chemical fertilizers used for the agriculture.

Tritium analysis was also performed for the same set of samples to determine the residence time of groundwater. The relation between tritium concentration and electrical conductivity and elevation shown in Fig. 7, reveals that the karstic springs are mostly recharged via sinkholes in the region. As seen in Tab. 1 and Fig. 7, the tritium values range between 6.62 and 6.69 TU for surface waters and between 5.28 and 5.95 TU for the karst springs. This result indicates the relatively short residence time of water in aquifer system.

#### TRACER TEST

The uranine tracer test was also performed to investigate possible connections between the sinkholes and springs. Subatan sinkhole was selected as the artificial tracer injection point and some big springs such as SP5, SP6, and SP8 were selected as monitoring points as shown in Figs. 2 and 9. About one kg of uranine was injected into the surface water at SP2 point, which flowed into the Subatan sinkhole (Fig. 2). Uranine concentration was measured at sampling points SP5, SP6, and SP8 at 15 minute intervals. Uranine was detected only at the SP6 sampling point, which has the highest flow rate in the south of the



Fig. 7: Scatter diagram of the tritium, electrical conductivity and elevation.



Fig.8: Uranine concentration in SP6 sampling location.

study area. The concentration was low, reaching 0.3 ppm at its maximum. The water emerges from the mica-schist fracture zone and mix a with Pitrak stream controlled by N-S running fault system as shown in Fig. 3. Uranine was not detected at SP5 and SP8 sampling points, which are located in Camyayla polje in the west of the study area (Fig. 3). This indicates that the groundwater flow is controlled by N-S directed fault system in the marble unit and the water from Camyayla polje has a different flow direction. The peak uranium concentration was detected after ten hours from the tracer being injected in to the Subatan sinkhole (Fig. 8). The tracer test demonstrates that the contribution to the sinkhole on the discharge of SP6 is small but there is a link between sinkholes and karst springs which are 4 km away from each other. Apparent flow velocity was estimated to be 400 m/h. A set of photographs given in Fig. 9 shows the karst features in sinkholes. Based on the speleological studies in the sinkholes, the karst conduit system is found to be fairly complex and it is considered that after the siphons, the big portion of groundwater flows through the fault/conduit system toward the south of the graben system as seen in the conceptual model in Fig. 10.

#### CONTAMINANT TRANSPORT AND PROTECTION ZONE OF KARST FEATURES

The inflow to the Subatan sinkhole is 10 times higher than the inflow to the Ayvacik sinkhole. As seen in Fig. 4, the dimensions of Subatan sinkhole are large and therefore the sinkhole has relatively large capacity. The chemical, isotopic, and tracer analysis showed that the surface waters at Ayvacik and Subatan Poljes drain into the marble aquifer through these sinkholes. In addition, the flow mechanism is also explained by comparing the toxic ions content of the surface and spring waters in marble karst system, such as nitrate and arsenic, as show in Tab. 1. Arsenic and nitrate concentrations are above the standart values at sampling points SP2 and SP6, which are interconnected via the sinkhole. Ayvacik and Subatan poljes are mainly effected by the agricultural activities, including ranching and chemical fertilization. Result indicates that mixing of sinkholes with groundwater contributes to an increase in the toxic element concentration at SP6 spring point. Therefore, Ayvacik and Subatan sinkholes should be protected from the agricultural activities as several springs discharging from the marble aquifer are used for drinking purposes in the study area.



Fig. 9: A series of pictures from sinkhole to spring (a: Subatan sinkhole, b and c: caves and karstification in marble, d; Pıtrak Spring).



Fig. 10: Conceptual groundwater flow mechanism in the marble aquifer in the study area.

## CONCLUSION

Menderes Metamorphic units mainly composed of mica-schist with massive thin bedded marble layers are the main base rocks in the Western Anatolia. Highly fractured and karstified dolomitic marbles of the Bozdag Mountain represent the main karstic aquifer in the Menderes Massive. Ayvacik and Subatan enclosed poljes were developed by N–S running deep faults system and are drained by Ayvacik and Subatan sinkholes. Marble karstification was explored down to 240 m based on speleological observations in Ayvacik and Subatan sinkholes. Three karstification zones were classified within the Ayvacik sinkhole, which evolved along N-S trending faults. Large karst features observed in massive marble include shafts and galleries with vertical walls in the first section that runs down to 100 m from the surface. Several narrow shafts and galleries with low slope angles were observed in the second section between 100 m to 200 m from the surface. The third section goes down to 239 m and ends with a siphon.

Chemical analyses show that the enrichment in Ca and Mg ions were due to dissolution in the marble aquifer. Ions such as arsenic and nitrate were detected above the drinking water standard levels, both in the surface SP2 and in the spring water at SP6. Thus, the marble aquifer in the study area should be protected from the agricultural activities especially in the polje drainage area and chemical fertilizer use should be reduced to a minimum value, in order to minimize the degradation of the water quality. It is important to note that the Menderes Massive rocks are widespread in the western Anatolia region and that the marble aquifers within this massive are typically utilized to obtain high-quality water in large quantities.

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