



# RESERVOIR-TARGETED OIL AND GAS EXPLORATION IN THE KARABURUN PENINSULA (WESTERN TURKEY)

Adil Ozdemir<sup>1,\*</sup>, Atilla Karataş<sup>2</sup>, Yildiray Palabiyik<sup>3</sup>, and Alperen Sahinoglu<sup>3</sup>

<sup>1</sup> Adil Ozdemir Engineering & Consulting, Ankara, Turkey.

<sup>2</sup> Department of Geography, Faculty of Arts and Sciences, Marmara University, İstanbul, Turkey.

<sup>3</sup> Department of Petroleum and Natural Gas Engineering, Faculty of Mines, İstanbul Technical University, İstanbul, Turkey.

<sup>4</sup> Institute of Science and Technology, İstanbul Esenyurt University, İstanbul, Turkey.

\*Corresponding author e-mail: adilozdemir2000@yahoo.com

## ABSTRACT

In recent years, it has been determined to exist mature petroleum hydrocarbons in the Karakaya complex units which broadly spread over Northern Turkey and some of the Upper Paleozoic and Triassic sediments in the Karaburun Peninsula have shown similarity with the sandstones of the Karakaya complex. Besides, there are mercury deposits that were operated in the Karaburun Peninsula in the past and the surface and subsurface waters in the regions where mercury deposits are located contain high concentrations of mercury. It is known that the formation waters of gasfields contain high concentrations of mercury as well. For these reasons, in this study, it is aimed to investigate the oil and gas potential of the Karaburun Peninsula by conducting Total Petroleum Hydrocarbons (TPH) analysis on the samples taken from the water resources. As a result of the analyses conducted, the hydrocarbons have been detected in all the water samples. The organic geochemical methods have been used to determine the source of hydrocarbons detected in the water resources. The detected nalkane hydrocarbons are the mature petroleum hydrocarbons and the presence of these hydrocarbons is evidence for the existence of a working petroleum system in the study area. The main structure in the maximum depth of 220 m determined in the study area has a very high potential to become an oil and/or gas reservoir according to gravity and magnetic data and because of the presence of waters containing mature petroleum hydrocarbons.

**Keywords**: reservoir-targeted oil and gas exploration, TPH in water analysis, hydrocarbon-rich water, mercury deposit, mercury mineralization.

## **1. INTRODUCTION**

The study area is a tectonic belt located in the southwestern edge of the Bornova Flysch Zone [1,2] in the İzmir-Ankara Zone [3]. In Karaburun Peninsula, there is a relatively





regular Paleozoic and Mesozoic aged autochthonous sequence and various tectonostratigraphic units with an allochthonous position. The Paleozoic aged unit in the lowest of the autochthonous sequence is composed of Cambrian (?) - Ordovician clastic rocks and is turbiditic. This unit is overlain by Silurian-Carboniferous and Visean-Bashkirian clastic and carbonate rocks cutted by Early Triassic Karaburun granodiorite [4]. Karaburun is a peninsula in Western Turkey where a quite thick carbonate sequence takes place. Mesozoic carbonates present a thick sequence from Early Triassic to Late Cretaceous. The upper levels of the basement rock units continue with a Middle Triassic-Late Cretaceous carbonate sedimentary sequence [4,5]. Neogene is seen as a volcano-sedimentary series overlying the basement units [4,6]. Quaternary alluviums cover these units in various areas of the peninsula (Figure 1).

Ozdemir and Palabiyik [7-10] have stated that metallic ore deposits, which are capable of forming deposits in operable-size, are a shallow and trustworthy indicator for the oil and gas accumulations. There are mercury deposits in the Karaburun Peninsula that were operated formerly (Figure 1). All the major mercury deposits in Turkey are epithermal and was occurred in the depths varying from 1 to 600 m by the upwelling of hot fluids (50°C to 200°C). The ore is located in veins or disseminated in sandstones and schists [11]. Oil or bitumen has been determined in the mercury deposits [12-15]. Bailey [16] and Shabo et al. [17] suggested that cinnabar (HgS) and bitumen were precipitated by a common fluid. The presence of bitumens along with mercury ores has led to the assumption that mercury is precipitated by organic matter. However, in many cases, mercury appears together with oil rather than solid bitumen [18]. Chakhmakchev et al. [19] stated that mercury is enriched in light oil and many other metals in heavy oil. Mueller [12] suggested that near-surface and low-pressure conditions valid for mercury mineralization are suitable for the accumulation of a series of organic deposits unique for this kind of mineralization. The maximum concentrations of bitumen (sensu stricto) in organic matter have been determined to be associated with the highest mercury content mineralization. Mercury is abundant in oil and gas fields and an important data used for hydrocarbon exploration [18,20,21].

In particular, formation waters of gasfields contain high amounts of mercury [20]. Gemici [11] and Gemici and Oyman [22] have determined that the surface and subsurface waters in the Karaburun Peninsula, especially in the regions where mercury deposits are present, contain high amounts of mercury as well. Groundwater samples are approximately neutral-alkaline (pH: 7.3 to 7.5). The pH values of the waters in Kalecik mercury deposit and its surroundings are ranging from 4.4 to 8.4 [22]. While Hg concentrations of groundwater samples are 0.001 to 0.13  $\mu$ g/L, Hg contents of the waters passing through the mercury mine and leaving the gallery are 0.01 to 0.99  $\mu$ g/L [11]. The permissible limit value for Hg contents of waters in the "Water Pollution Control Regulation of Turkey" is 0.1  $\mu$ g/L.







Figure 1. Geological map of the study area (modified from [1-6]).

There are operable-size mercury deposits in Karaburun Peninsula. In recent studies, the presence of mature petroleum hydrocarbons in Karakaya complex units which present widespread distribution in Northern Turkey [23,24] and some similarities between the Upper Paleozoic and Triassic sediments of the Karaburun Peninsula and the sandstones of Karakaya Complex [25,26] has been determined. Therefore, in this





study, the main target is to investigate the oil and gas potential of Karaburun Peninsula by Total Petroleum Hydrocarbons (TPH) analyses conducted on the samples taken from some water resources carefully selected in the region. The study was carried out in three stages. In the first stage, the geological characteristics of the study area have been examined from the literature. Thus, the geological data required for geochemical analyses and geophysical evaluations have been compiled. In the second stage, magnetic and gravity maps of the study area have been prepared. In the third and final stage, as a result of the joint evaluation of the geological and geophysical data, TPH in water analyses have been performed on the samples taken from the selected water resources in the study area and its surroundings. According to the consequences of the analyses, the mature petroleum hydrocarbons have been detected in all the water samples. These mature hydrocarbons can be regarded as a strong evidence for the existence of a working petroleum system in the investigation area.

# 2. MATERIAL AND METHOD

Eymold et al. [27] have determined that shallow groundwaters above the basin formations containing shale gas are enriched in hydrocarbons. They have also expressed that the hydrocarbons in these hydrocarbon-rich waters migrated from deep source rocks to shallow aquifers. Moreover, Kreuzer et al. [28] have mentioned that the faults in petroliferous basins make the transportation of hydrocarbon-rich brines to aquifer formations above source rocks easy by influencing the geochemistry of shallow groundwaters and cause a hydrocarbon enrichment in these waters. Dultsev and Chernykh [29] have stated that it is a very good geochemical tool for oil and gas exploration of hydrocarbon-rich waters around hydrocarbon accumulations in the subsurface.

On the other hand, in recent times, TPH in water analysis has started to be utilized in petroleum exploration, which allows the determination of hydrocarbon-rich waters and organic geochemical properties in basins/regions where source rocks are not exposed at the surface as outcrops (covered basins) or has been exhausted (depleted or spent) [30-32].

Furthermore, in recent studies, it has been come into existnce that all organic geochemical analyses conducted on source rock and gas samples can also be applied to hydrocarbon-rich surface and subsurface waters determined by TPH in water analysis and that the same analysis and interpretation results for the same basins/regions have been reached (Figure 2) [33,34].

According to these studies, if an oil and/or gas reservoir exists in a region, the surface and subsurface waters in the study area should be rich in mature petroleum hydrocarbons (Figure 3). Therefore, it can be inferred that the technique of TPH analysis in water will significantly contribute to reservoir-targeted oil and gas exploration activities.





TPH value provides information on hydrocarbon contamination of water resources. Gas chromatography (GC) analyses are performed to detect the TPH concentrations of the water contaminated by hydrocarbons. In the determination of TPH content, the standard test method "the Determination of Hydrocarbons: Solvent extraction and gas chromatography method (ISO 9377-2)" is used (other methods: EPA Method 1664 and ASTM D7678-11). In this technique, aromatic hydrocarbons are separated, and the total amount of petroleum hydrocarbons is determined in the samples taken from the surface, subsurface, and distribution waters.

These samples are stored by an acidification process to prevent the issues, which may affect the number of hydrocarbons, such as evaporation or biodegradation in the samples. Samples are analyzed within 14 days if acidified, or they are performed within 7 days if not done, and stored at  $5^{\circ}C \pm 3^{\circ}C$  before the analysis.

In the comprehension of this research, totally 23 samples have been taken by the scaled polyethylene bottles of 1 liter from the natural flowing waters (cold water fountains) in the region (Figs. 4 and 5). The water samples are taken from the untreated water resources that are not related to tap water (running water). Since the water samples collected from the study area have been analyzed a few days after the sampling, no acidification process has not applied to the samples. They were collected and preserved according to the standard procedures (ISO 5667-3) and analyzed in the laboratory for TPH in water employing the standard methods (ISO 9377-2). In the samples, the TPH analyses have been conducted by a gas chromatography device in the laboratory to generate data for organic geochemical evaluations.

Thus, direct TPH concentrations of the water samples (in mg/l) have been determined depending on the analyses and the required geochemical parameters (CPI, NAR, etc.) to be discussed in detail in the next section of the paper have been calculated by making use of gas chromatograms. In the geochemical evaluations, the TPH concentrations and the calculated parameters are used.







**Figure 2.** Ph/n-C18 vs Pr/n-C17 ratios of deep groundwater and rock samples taken from the same region [34] (Pr: Pristane and Ph: Phytane isoprenoid hydrocarbons, nC17 and nC18: n-alkane hydrocarbons).



**Figure 3.** Components of an anticlinal type of petroleum reservoir that can be produced by primary methods [33].







**Figure 4.** Location map of the formerly operated mercury mines (red stars) and the water samples (yellow circles) taken from the Karaburun Peninsula.



**Figure 5.** A view of water samples taken from water resources in the study area by using scaled plastic bottles.

## 3. FINDINGS AND DISCUSSION

Based on the TPH analysis results regarding the water samples taken from the study area, concentrations, biodegradation conditions, source, maturity, and redox conditions of the depositional environment of the hydrocarbons in the waters are





investigated in a geochemical point of view. Moreover, the aeromagnetic and gravity maps prepared for the study area are interpreted in terms of geological and tectonic aspects, and the construction of the conceptual occurrence, migration, and accumulation model of the hydrocarbons is targeted.

# 3.1. Content, Source, and Biodegradation Condition of Hydrocarbons in Waters

Liu et al. [34] have defined groundwater whose hydrocarbon concentration is greater than 0.05 mg/L as original hydrocarbon-rich groundwater. n-alkane kinds of hydrocarbons were detected in all the water samples in the study area. The hydrocarbon content of the water samples is significantly higher than the limit values recommended for groundwaters (Tables 1 and 2). Thus, water-rock-hydrocarbon interactions have caused hydrocarbon enrichment in water.

The main parameters affecting in the hydrocarbon compositions are source, maturity, migration, and biodegradation. Ph/n-C18 value less than 1 indicates non-biodegraded hydrocarbons [35] and Ph/n-C18 values of all the water samples are less than 1 that indicates the non-biodegraded hydrocarbons in the water samples.

By using gas chromatography analyses results, the Carbon Preference Index (CPI), Pristane/Phytane ratio (Pr/Ph), isoprenoid/n-alkane ratio (Pr/n-C17 and Ph/n-C18) are calculated, and n-alkane distributions are assessed. In this study, Pr/Ph ratio, Carbon Preference Index (CPI), Pr/Ph versus CPI, and Pr/n-C17 versus Ph/n-C18, Pr/n-C17 versus Pr/Ph plots are utilized to assess the water samples.

TPH (mg/L)	References
< 0.05	[34]
< 0.1	[36]
< 0.5	[33]
< 0.2	[37]
< 0.02	[38]

**Table 1.** Recommended TPH limit values for surface and subsurface waters

CPI is an indicator of the source of n-alkanes and a ratio between the amounts of nalkanes having odd and even carbon number, is calculated by measuring the heights of the peaks in gas chromatograms. The dominant peaks in these chromatograms are n-alkanes. In the computation of the CPI, different formulas were suggested by various researchers. This index can be applied to any range of the carbon sequence and used to assess the type of organic matter, the sedimentation environment, and thermal maturity.

Based on whether this value is markedly higher than 1 (odd n-alkane preferential) or less than 1 (even n-alkane preferential) indicating thermally immature oil or bitumen samples [43,44]. A high CPI value in the immature or low-maturity sample reflects the input of organic matter derived from higher terrestrial plants [45]. According to CPI





values (Table 2), the source of n-alkanes in the water samples is petrogenic hydrocarbons and older organic-rich sediments (Table 3).

Commlo		Coordinates		TPH	CPI	TAR	NAR	Pr/Ph	Pr/n-	Ph/n-
Sample	Water			(mg/L)					C17	C18
INO.	resource	Х	Y							
K-1	NFW	4277145	456402	0.71	2.10	8.23	0.08	16.14	0.23	0.05
K-2	NFW	4275504	455389	0.49	1.96	9.95	0.00	27.43	0.25	0.03
K-3	NFW	4273440	455160	< 0.40	1.50	-	0.13	5.25	0.34	0.12
K-4	NFW	4270918	454154	0.56	1.31	12.54	0.23	7.44	0.27	0.08
K-6	NFW	4269788	452357	0.63	0.73	4.62	0.33	1.47	0.15	0.22
K-7	NFW	4264088	446995	0.78	0.77	5.29	0.35	3.78	0.13	0.09
K-8	NFW	4261512	449740	0.59	1.84	-	0.13	0.60	0.06	0.29
K-10	NFW	4260808	448936	0.54	1.34	6.66	0.25	2.20	0.15	0.16
K <b>-</b> 11	NFW	4261399	448140	0.52	1.36	8.12	0.34	1.19	0.13	0.27
K-13	NFW	4268255	446176	0.51	1.12	4.99	0.30	0.65	0.05	0.21
K-14	NFW	4272415	446349	0.57	1.45	7.26	0.30	1.40	0.09	0.17
V 16	Caisson	4273824	447640	0.54	1.03	-	0.39	2.47	0.18	0.16
K-10	well									
K-17	NFW	4277986	447547	0.63	1.42	5.92	0.32	0.92	0.06	0.20
K-19	NFW	4279481	449949	0.58	1.41	5.39	0.34	1.22	0.08	0.17
K-20	NFW	4278749	453788	0.71	1.60	7.23	0.05	1.23	0.06	0.11
K-21	NFW	4274163	458235	0.78	1.92	5.24	0.01	0.88	0.04	0.13
K-23	NFW	4267760	462752	0.52	1.15	6.96	0.30	4.52	0.21	0.11
K-24	NFW	4267018	463233	0.64	1.16	7.33	0.37	5.04	0.19	0.09
K-25	NFW	4266250	462648	0.61	0.74	-	-	0.14	0.08	1.07
K-27	NFW	4266499	462141	0.57	1.76	-	-	1.27	0.14	0.05
K-28	NFW	4266689	461004	0.52	1.09	6.45	0.35	27.20	0.25	0.02
K-29	NFW	4264656	460776	0.54	1.18	9.37	0.32	2.27	0.06	0.05
K-30	NFW	4258707	460868	0.47	-	6.50	-	0.48	0.02	0.08

**Table 2.** TPH analysis results of the water samples and the calculated parameters

NFW: Natural flowing water, CPI = {[(C23+C25+C27) + (C25+C27+C29)] / [2 \*(C24+C26+C28)]} [39,40], TAR = (C27+C29+C31)/(C15+C17+C19) [41], NAR = [ $\Sigma$ n-alk (C<sub>19-32</sub>) - 2 $\Sigma$  even n-alk (C<sub>20-32</sub>)] /  $\Sigma$  n-alk (C<sub>19-32</sub>) [42], - : Could not be calculated.

The term "petrogenic resources" represents unburned fossil resources such as crude oil and coal formed very slowly at moderate temperatures (between 100 °C and 300 °C) millions of years ago [46]. The NAR (Natural n-alkane Ratio) parameter is come up with to interpret the source of hydrocarbons in the related environment (natural or petroleum n-alkane) [42]. and zero or approximate to zero for petroleum hydrocarbons and crude oil. In other hydrocarbon resources, it is higher and all the n-alkanes in the water samples are natural petroleum (petrogenic) hydrocarbons as can be seen in Table 2.





TAR (Terrestrial/aquatic hydrocarbon ratio) reflects the ratio of n-alkanes derived from terrestrial organic matter to n-alkanes derived from aquatic algae [41,47-49] and these values are calculated as quite high for the inspected water samples (Table 2) by indicating that n-alkanes with high carbon numbers representing terrestrial organic matter are dominant in the water samples.

**Table 3.** Source of n-alkanes in water according to CPI value [33]

CPI	Source
> 2.3	Young terrestrial sediments
	(biogenic hydrocarbons)
1.2 -	Old organic-rich sediments
2.3	(marine shales, limestones, etc.)
≤1.2	Petrogenic hydrocarbons
	(< 1 values is biodegragation oils)

**Table 4.** Maturity levels of hydrocarbons according to CPI value<br/>(from [50]) (see Figure 6)

CPI	Maturity
>1	Mature (oxidizing-reducing)
0.8 - 1	Mature
< 0.8	Immature

n-alkanes which are the closest to isoprenoids in gas chromatograms have been used in isoprenoid/n-alkane ratios. Pr/Ph ratio is a good correlation parameter. Although pristane (Pr) and phytane (Ph) define other sources, they are derived from phytyl which is the side chain of chlorophyll, especially in phototropic organisms. Under anoxic conditions, the side chain of phytyl breaks down to form the phytol while phytol is also reduced to pristane under oxic conditions [44]. Thus, Pr/Ph ratio reflects the redox potential of the deposition environment. Pr/Ph values less than 1 indicate anoxic conditions whereas the values greater than 1 indicate oxic conditions [35,51]. A Pr/Ph ratios ranging from 0.14 to 27.43 in water samples were calculated. Hence, some of the water samples were found hydrocarbons derived from sediments deposited in an anoxic environment (Pr/Ph < 1) and some of the other samples correspond to an oxic environment (Pr/Ph > 1) (Table 2). The Pr/Ph ratio also provides information about paleoenvironment and maturity level [52]. In the Pr/Ph-CPI diagram, it can be seen that the hydrocarbons in the water samples are located in the more oxidizing zone and have the similar maturity levels (Figure 6).

Pr/n-C17 and Ph/n-C18 ratios are commonly utilized in petroleum correlation studies. High levels of oxidation of samples are determined to indicate an oxidizing source while the high phytane content reflects a reducing source. Therefore, the diagrams of Pr/n-C17 vs Ph/n-C18 were used to classify petroleum or bitumen in different groups [35]. The Pr/Ph ratio above 1.5 indicates that the Pr/Ph ratios may be





less than 1 for anoxic deposition environment although they indicate settling conditions in an oxygenated environment according to a standard geochemical interpretation. Lower values may demonstrate less oxic conditions than the other parts of the same sequence [53]. The ratio of isoprenoid/n-alkane decreases with the increase in maturity as more amounts of n-alkanes release from kerogen subjected to a breaking down phenomenon [35,43] and is used as a measure of maturity for biodegradable oil and bitumen samples. This ratio increases with the biodegradation [35], and is also affected by organic matter input and secondary processes. According to their positions in the Pr/n-C17 vs Ph/n-C18 diagram of the water samples, it is observed that the source rocks which generated the hydrocarbons in the water samples were come up with to deposite in anoxic marine (Type-III kerogen), anoxic-suboxic transitional (Type II-III kerogen), and oxic terrestrial (Type-III kerogen) environment and the hydrocarbons are featured in the mature-overmature level (Figs. 7-10 and Table 5).



Figure 6. Pr/Ph vs CPI plot of the water samples (the plot: from [50].



Figure 7. Pr/n-C17 vs Ph/n-C18 plot of the water samples







**Figure 8.** Pr/n-C17 vs Pr/Ph plot of the water samples (the plot: from [55-57]).



Figure 9. Ph vs Pr plot of the water samples (the plot: from [58]).







Figure 10. CPI vs Pr/Ph plot of the water samples (the plot: [59]).

Table 5. Source rock and deposition environment of hydrocarbons according
to Pr/Ph value (from [58]) (see Figure 9).

Pr/Ph	Source rock	Pr/Ph	Environment
< 3	Marine	< 0.8	Anoxic
3 - 5	Marine - Terrestrial	> 0.8	Suboxic-Oxic
> 5	Terrestrial		

# 3.3. Aeromagnetic and Gravity Maps of the Study Area and Geological Interpretations

Numerous studies exist in the literature regarding the techniques and their usage of field applications of gravity and aeromagnetic data for use in oil and gas exploration [30-32, 60-69]. Analysis of gravity and magnetic anomalies has been a permanent component of hydrocarbon exploration and discovery in West Siberia for half a century [66]. In the regions where the presence of mature petroleum hydrocarbons (determined hydrocarbon-rich waters) is proved in this study, especially seismic surveys are critical to determine the locations of oil and gas reservoir(s)/trap(s). However, no seismic lines/measurements are available in the study area. The contour maps specifically were prepared for the surveyed region from regional gravity and aeromagnetic data measured by General Directorate of Mineral Research and Exploration of Turkey (MTA) were used to evaluate the subsurface geology of the study area.

The gravity map prepared for the study area (Figure 11) contains young sediments composed of lower-density sedimentary origin rocks (siltstone, mudstone, claystone, conglomerate, shale, etc.) and metamorphic (slate, phyllite, etc.) rocks represented by dark blue, light blue, and green colors. In the areas featured by orange, red, and yellow



colors, an anomaly is exhibited by the rocks having relatively higher densities (crystallized limestone, marble, quartzite, schist, etc.). In the study area, there is a thick carbonate rock sequence which is expected to have high density. However, the gravity of carbonate rocks is lower than the expected values. This situation should have been caused by epigenetic processes and secondary alteration (Figure 11).

The prepared aeromagnetic map for the study area (Figure 11) covers fully nonmagnetic sedimentary (sandstone, limestone, siltstone, mudstone, claystone, conglomerate, shale, etc.) and metamorphic (crystallized limestone, marble, quartzite, schist, etc.) rocks represented by blue, green and light yellow colors in the map prepared. In the areas represented by yellow, orange, red, and white colors, there are the rocks with magnetic properties (volcanic pebbly sandstones, ophiolites, dikes, etc.). In the study, the interpretation method proposed by Svancara [70] and Töpfer [71] have used to convert the 2-D (two-dimensional) residual gravity anomalies into the depth values and determine the basin and structure depths. In this method, if the density contrast is known, the depth of the sedimentary basin or structure can be calculated by simple relations established between gravity anomaly and parameters. The first step of the interpretation yields the characteristic parameters of the anomaly (Figure 12). The related equations can be written as follows:



**Figure 11.** The colorful contour maps and geological interpretations of the regional gravity (a) and aeromagnetic (b) anomalies of the study area. Possible oil trap: red polygons, white lines: strike-slip faults, blue lines: thrust faults, A-B is the profile taken to determine the maximum depth of the structure (see Figure 14).





(1)

$$A = \frac{g_{max}}{W_a \sigma}$$

 $g_{max}$ : Maximum amplitude of the gravity anomaly (mgal),

 $W_a$ : Distance corresponding to the half amplitude  $(g_{max}/2)$  value of the gravity anomaly (m),

 $\sigma$ : Density contrast (gr/cm<sup>3</sup>).

$$\frac{W_b}{W_a} = (-0.056A) + 1.827 \tag{2}$$

$$D_o = 23.866 \frac{g_{max}}{\sigma} \tag{3}$$

For the condition  $0 \le A \le 9$  [71]:

$$\frac{D}{D_o} = 0.072A + 1.00$$
 (4)

For the condition 9 < A < 13 [71]:

$$\frac{D}{D_o} = 0.12A + 0.57$$
 (5)

Where

 $W_b$ : Full width of the gravity anomaly (m),

*D<sub>i</sub>*: Depth corresponding to the gravity anomaly value (mgal),

 $D_0$ : Depth obtained from the flat-plate formula (m),

D: Maximum depth (m).

An A-B profile was obtained from the residual gravity anomaly map of the study area (Figure 11). According to the anomalies of the A-B profile, the maximum depth of the structure (D) was calculated to be 220 m (Figure 13).



**Figure 12.** Ideal gravity anomaly of a basin and characteristic parameters [70].

The mature hydrocarbons are evidence for a working petroleum system in the study area. Possible oil/gas reservoir in study area is a thrust anticline which is determined by gravity and magnetic maps which are highly compatible with each other and limited by strike-slip faults where they are predominantly in the NE-SW orientation and the hydrocarbons can be trapped and protected (Figs. 11 and 13). The fact that the structures are between the two thrust zones makes the possibility of hydrocarbons being deposited stronger in these structures. The hydrocarbons in the water samples must have migrated from the possible reservoir(s) (Figure 14) determined by gravity





and magnetic maps to the surface/near-surface and mixed with shallow water resources.



**Figure 13.** Geological interpretation of A-B profile and depth of potential oil and/or gas reservoir in the study area (see Figure 11).







**Figure 14.** Potential oil and/or gas traps (red polygons) in the study area. Yellow circles: the water samples containing mature petroleum hydrocarbons, pink stars: formerly mercury mines, white lines: strike-slip faults, blue lines: thrust faults. A-B line: taken profile to determine the depth of structure (see Figure 11).

Senger et al. [72] have investigated the effects on petroleum systems of magmatic intrusions. The main components of a petroleum system are as follows: (1) conditions leading to the hydrocarbon generation, (2) the ways that hydrocarbons that migrated from the source rock can migrate, (3) a porous and permeable rock acting as a reservoir for hydrocarbons, (4) low-permeable peripheral rock units and (5) a covered structure (trap). Magmatic intrusions can affect anyone or several of these five major components of the petroleum system. Jointed and permeable magmatic intrusions can create new migration paths, or act as a fluid barrier when they are crystallized and impermeable [72]. With the effect of these magmatic activities, hydrocarbons-rich waters can be transported from the oil reservoirs to the surface and mix with different origin waters (meteoric water, seawater, etc.). The settlement of Karaburun granodiorite [73] and intensive volcanic activities in the Karaburun Peninsula [6] are also thought to be effective on maturing of hydrocarbons in the water samples.

# 3.4. Conceptual Occurrence, Migration and Trapping Model of Hydrocarbons in the Study Area

The understanding of the occurrence of petroleum source rocks is critical in oil and gas exploration. The factors controlling the occurrence and accumulation of the petroleum source rocks are related to the events and changes such as dynamics, chemistry, biology, etc. of an ocean system that have taken place through geological time. On the sedimentation in the Tethys Region, there is a great control of the





paleogeographic location and the tectonic past, which has led to the formation, migration, and closure of hydrocarbons in the region. Ozdemir and Palabiyik [74,75] have mentioned that petroleum source rocks were formed in the mid-ocean ridges and in the continental rifts (spreading centers). Therefore, the source rocks that derived hydrocarbons in the water samples should have formed in the geological period(s) containing rifting processes in the study area. Karaburun Peninsula was exposed to rifting during both Upper Silurian and Lower Triassic periods and formed the rift basins (Figure 15). In the study area, the source rocks that derived the hydrocarbons should have been formed in the rift basins developed as a result of these two rifts because the hydrocarbons in the water samples were derived from both marine, transitional, and terrestrial source rocks (Figs. 7-10).



Figure 15. (a) Upper Silurian (420 Ma) and (b) Lower Triassic (245 Ma) paleogeography of Turkey (Ruban et al., 2007).





Paleozoic - Lower Tertiary units in the north of the Karaburun Peninsula give an idea about the tectonic evolution of Tethys ocean. The northwest of the Karaburun Peninsula is dominant with a thick melange with Silurian - Carboniferous blocks (up to hundreds of meters in size) with neritic and pelagic limestone, black banded chert, shale, magmatic intrusions and volcanogenic sediments, and large amounts of shear zones. This melange is unconformably covered by Lower Triassic rifting units containing terrestrial clastics, pelagic carbonate, radiolarite, lava, and volcanogenic sediments. In the region, there are shallow and wide Mesozoic carbonate platform facies formed in different periods. The deposition in the Karaburun Peninsula has been interrupted by local deltaic siliciclastic deposition that emerged during the Upper Triassic and Lower Jurassic periods. The Karaburun carbonate platform later emerged, eroded, and collapsed during the Campanian-Maastrichtian period. During the Maastrichtian - Lower Tertiary period, it was covered by another mélange (Bornova Melange) containing blocks belonging to Mesozoic oceanic lithologies, which was rundowned and derived from the local platform. In the last stage, during the continental collision, it has taken the form of the accretionary prism (Figure 16) [73].

*a. Ocean formation and marine sedimentation:* Near the platform, it begins with a new seafloor spreading center (mid-ocean ridge) and oceanic crust formation. This crust consists of fractional melting of the mantle, formation of magma chambers, vertical dyke injection, and volcanic extrusion at the ocean floor and a series of magmatic rock groups formed at various depths under the mid-ocean ridge. As the ocean continues to open, marine sediments accumulate on the shelf, on the slopes, on the tops of the platform, and on the abyssal plain of the new ocean. Deep oceanic sediments include radiolarian cherts, fine muds, coarse-grained, shelf-edge, and turbiditic discharge sediments on the slope deposited as a result of submarine landslides in the areas close to the platform. Isolated limestone banks or coral atolls were developed offshore on seamounts (extinct subsea volcanoes) and on the foundered ridges created in association with the early stages of ocean rifting. According to Ozdemir and Palabiyik [75], the oil should have occurred at this stage.

*b. Plate subduction:* Between platform and mid-ocean ridge, a subduction zone develops. The plate carrying the platform begins to plunge under oceanic crust along the deep oceanic trench.

*c. Obduction of the ophiolite and starting of platform subduction:* The subduction process continues until the platform is brought into the subduction zone. The subduction zone cannot accommodate relatively light (less dense) rocks that form the continental crust. Therefore, the arrival of the platform causes the subduction zone area to be the jam. In the final stage of the subduction-obduction process, the end portion of the platform is pushed under the obduction plate. However, the overriding plate consisting of upper mantle and oceanic crust force over the overlapping layers of deep ocean sediments the edge of the Platform that had accumulated in the trench. These sediments can deform as plastic and act as a lubricant layer. The settlement of the ophiolite nappe





causes to mountain formation. In addition, mantle rocks are occupied by hydrothermal fluids in their initial environment under the mid-ocean ridge along with during transferring and settlement. This causes the mantle rocks to transform into serpentine. According to geological units in the study area and the performed geochemical evaluations, the following stages can be proposed for the occurrence of source rock, migration, and trapping of hydrocarbons in onshore (Figure 17):

*d. The end of subduction and isostatic uplift:* After the initial obduction of the ophiolite nappe, a new subduction zone has been established and the subduction has ended. With the finale of the subduction, the thick overlapping rock assemblage that is accumulated by subduction and obduction process rises rapidly and isostatically because it has a lower density than the lower mantle. This uplift completes the detaching of the overlying ophiolite slice and possibly causes additional movement of the nappes in response to gravity. The mountain area on the platform rises and erodes rapidly, possibly with a relief isostatic uplift above sea level. Finally, young- and shallow-water sediments cover the mountains.

e. Regional uplift and erosion: Mountains are the consequence of the deformation of folding and thrusting. Subsequently, uplift and erosion are generally observed under arid or semi-arid conditions.







**Figure 16.** Tectonic evolution model of the Triassic rifting, passive margin collapse (Jurassic - Cretaceous), and collision deformation (Upper Cretaceous - Early Tertiary) phases in Karaburun Peninsula (modified from [73].





Plate Tectonics	Local Tectonics	Sketches	Folding, Faulting Uplift and Erosion Exotic Block	Petroleum Geology
collision	E Os Folding & Thrusting audu DO	s line	e. Regional uplift and erosion Post-obduction sediments New Subduction Zone Isostatic Rebound d. The end of subduction isostatic uplift	migration and
advanced closure of Tethys	Folding & Thrusting	T (3)	Syntectonic erosion and deposition Collapse of Obduction Internal thrust faulting Platform Edge of Ophiolite within Ophiolite Exotic Block Formation of Metamorphic Sole at base of Ophiolite c. Abortive subduction of the diaform and	trapping of oil
	Onset Deformation		obduction of the philothe Subduction Zone Overriding and development of	
onset closure of Tethys	General Subsidence	S L	b. Subduction of the plate	occurrence and
opening of Tethys	Carbonate Platform & Basin Formation	Carbonate Platform Basin S.L	Platform Tethys Ocean Mid-Ocean Ridge Continental Shelf Abyssal plain Seamount a. Ocean formation and marine sedimentation Platform Carbonates Ophiolite upper Mantie Upper Mantie Limestone	maturation of oil

**Figure 17.** The proposed conceptual model for occurrence of petroleum source rock and migration and trapping of oil in the study area (modified from 77-87).

## 4. CONCLUSION

In this study, based on the investigation of the oil and gas potential of Karaburun Peninsula by using TPH analysis performed on the samples taken from water resources, the hydrocarbons have been determined in all the water samples. The TPH values are significantly higher than the hydrocarbon limit values suggested for surface and subsurface waters. The source of n-alkanes in the water samples are petrogenic hydrocarbons and organic-rich and old sediments. Water-rock-hydrocarbon interactions have caused a hydrocarbon enrichment in the waters in the study area. It has been revealed that the hydrocarbons in the water samples are non-biodegraded. The source rocks which generated the hydrocarbons in the water samples were deposited in anoxic marine (Type-II kerogen), anoxic-suboxic transitional (Type II-III kerogen), and oxic terrestrial (Type-III kerogen) environment and are at the mature-overmature level.

The mature hydrocarbon-rich waters can be considered as a geochemical evidence for a working petroleum system in the investigation area in which there is a thick carbonate rock sequence which is expected to have high density. Nevertheless, the gravity values of carbonate rocks are lower than the expected ones. This situation





should have been caused by epigenetic processes and secondary alteration phenomenon. Thus, a high amount of mature hydrocarbons content in all the water samples according to geochemical analysis results together with gravity and magnetic data point out the existence of an oil and/or gas reservoir in the area. The asymmetric anticline, in which the hydrocarbons can be trapped and protected, determined by gravity and magnetic maps which are very compatible with each other, and limited by the strike-slip faults where they are predominantly in the NE-SW orientation, is the possible oil and/or gas reservoir in the region. To sum up, the fact that the structures are located between two thrust zones, increase the possibility of hydrocarbons being accumulated in these structures.

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