ISSN: 2717-7696
Research Article
Vol; 1, Issue; 2, pp. 35-52, 2020
DOI:
Journal homepage:
https://dergipark.org.tr/en/pub/turkgeo

Organic Geochemical Evidence of the Working Petroleum System in Beypazarı Neogene Basin and Potential Traps (Northwest Central Anatolia, Turkey)

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Keywords
Beypazarı Neogene basin,
Reservoir-targeted
Petroleum exploration,
TPH in water analysis,
Hydrocarbon-rich water,
Oil shale and coal

ABSTRACT
The Miocene units of the Beypazarı Neogene Basin extensively outcrop and prevalently include oil shale and coal. In the previous studies, it has been determined that the total organic carbon (TOC) values of bituminous shales in the basin are concentrated between 4-8% and algal organic matter (Type I-II kerogen) are dominant. It has also been determined that the bituminous shales have pyrolyzable hydrocarbon content of 83% and a potential source rock feature that can produce oil in a large quantity if exposed to high temperatures. Beypazarı Neogene Basin consists of volcano-sedimentary units. Therefore, as a result of the idea that the immature source rocks can be matured by young volcanic that exhibit widespread outcrops, it has been aimed to investigate the oil and gas potential especially in the northeastern part of the basin by TPH (Total Petroleum Hydrocarbons) analysis performed on the samples taken from the natural cold water resources located in the related part of the basin. As a consequence of the analyses conducted, 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 n-alkane hydrocarbons are the mature petroleum hydrocarbons derived from peat/coal type organic matter (Type III kerogen, gas-prone). The presence of these mature petroleum hydrocarbons is regarded as evidence for the existence of a working petroleum system in the study area. Due to the presence of waters containing mature petroleum hydrocarbons, the anticlines in the depth of approximately 110 m in fault-propagation folds identified in the investigation area by gravity and magnetic data have a very high potential to become gas reservoirs.

1. INTRODUCTION

The Beypazarı Neogene Basin, which commonly contains oil shale and coal, is located in the northwest of Ankara province (Figure 1). Regarding both interesting geology and economical value, lignite, gypsum, bituminous shale, clay, and trona deposits in the study area have been the subject of numerous geology targeted scientific studies in the literature until today. Coals and oil shales in the basin have been distinguished in many studies, and their formation environments, organic matter contents, and economic properties have been studied (Zieglar, 1939; Stchepinsky, 1941; Göktunalı, 1963; Aziz, 1976; Akkuş et al., 1982; Siyako, 1983; Yağmurlu et al., 1988a, b; Şener and Şengüler, 1991; Kavuşan, 1993; Şener et al., 1995; Özçelik, 2002; Özçelik and Altunsoy, 2005; Gülbay and Korkmaz, 2005, 2008; Şener, 2007; Toprak, 2010; Pehlivanlı, 2011; Vardaloğlu, 2016).

There are lignite seams in two stratigraphic levels in the Beypazarı Neogene Basin. The lower lignite seam is located at the lower levels of Çoraklar Formation while the upper lignite operated in Çayırhan Lignite Operation exists at the top levels of Çoraklar Formation (Figure 1). These units differ from the Hırka Formation with a characteristic contact. In the Koyunağılı lignite field, there is only the upper lignite seam (Figure 1). Lower lignite seams of Çoraklar formation present discontinuity in the lateral orientation. It was formed in the river environment and is completely different from the

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Received: 02/06/2020; Accepted: 28/06/2020

Cite this article

Ozdemir, A., Palabiyik, Y., Karataş, A., Sahinoglu A. (2020). Organic Geochemical Evidence of the Working Petroleum System in Beypazarı Neogene Basin and Potential Traps (Northwest Central Anatolia, Turkey). Turkish Journal of Geosciences, 1(2), 35-52.

upper lignite seam. The coals that make up the lower lignite level are generally characterized by blackish, locally banded, and matte colored soft lignites. The detectable thickness of the lower lignite level reaches up to 9 m. These coals, which are named as soft brown coal according to their physical properties, have a low calorific value (1700 kcal/kg). The upper lignite seam is laterally continuous and was formed in the mud plain facies of the playa-lake environment. The coals belonging to the upper lignite level are generally in dark brown and blackish, irregular bands, semi-gloss, and moderately hard. The total thickness of the upper lignite varies from 3.40 to 5.50 m and usually consists of two separate seams whereas the thickness of the coal seams of the upper lignite level varies from 1.40 to 2.10 according to the drilling and surface data. The calorific value of the upper lignite seam in the Çayırhan field was determined in the range from 3724 to 4602 kcal/kg while the calorific value of the lignite seam in the Koyunağılı field was measured as 2535 kcal/kg. The lignites in both fields are in uniform quality (Yağmurlu et al., 1988a). In the basin, 390 million tons of lignite reserves have been determined and Çayırhan Thermal Power Plant with a capacity of 620 MW power has been established in this area. Lignite seams outcropping in different thicknesses formed in the swampy environments of the lake basins in the Hırka Formation in different parts of the Beypazarı Neogene Basin have been identified. These lignites are called the plain basin type in terms of formation type (Toprak, 2010). The lignites of the Hırka formation exhibit different thicknesses. In the north and northwest of Beypazarı (Kabalar, Bahçeköy, Killikdere, Aşağıçay Dere, Sekili, and Hırkatepe), the thickness of the lignite veins ranges from 0.10 to 1.20 m (Özçelik, 2002; Toprak, 2010). In the Beypazarı Neogene basin, the coals in the Çayırhan region are named as Sector 1, and the coals between Çayırhan's coals in the Sector 1 and trona field are called Sector 2 (Figure 1) (Tarvirdi, 2013).

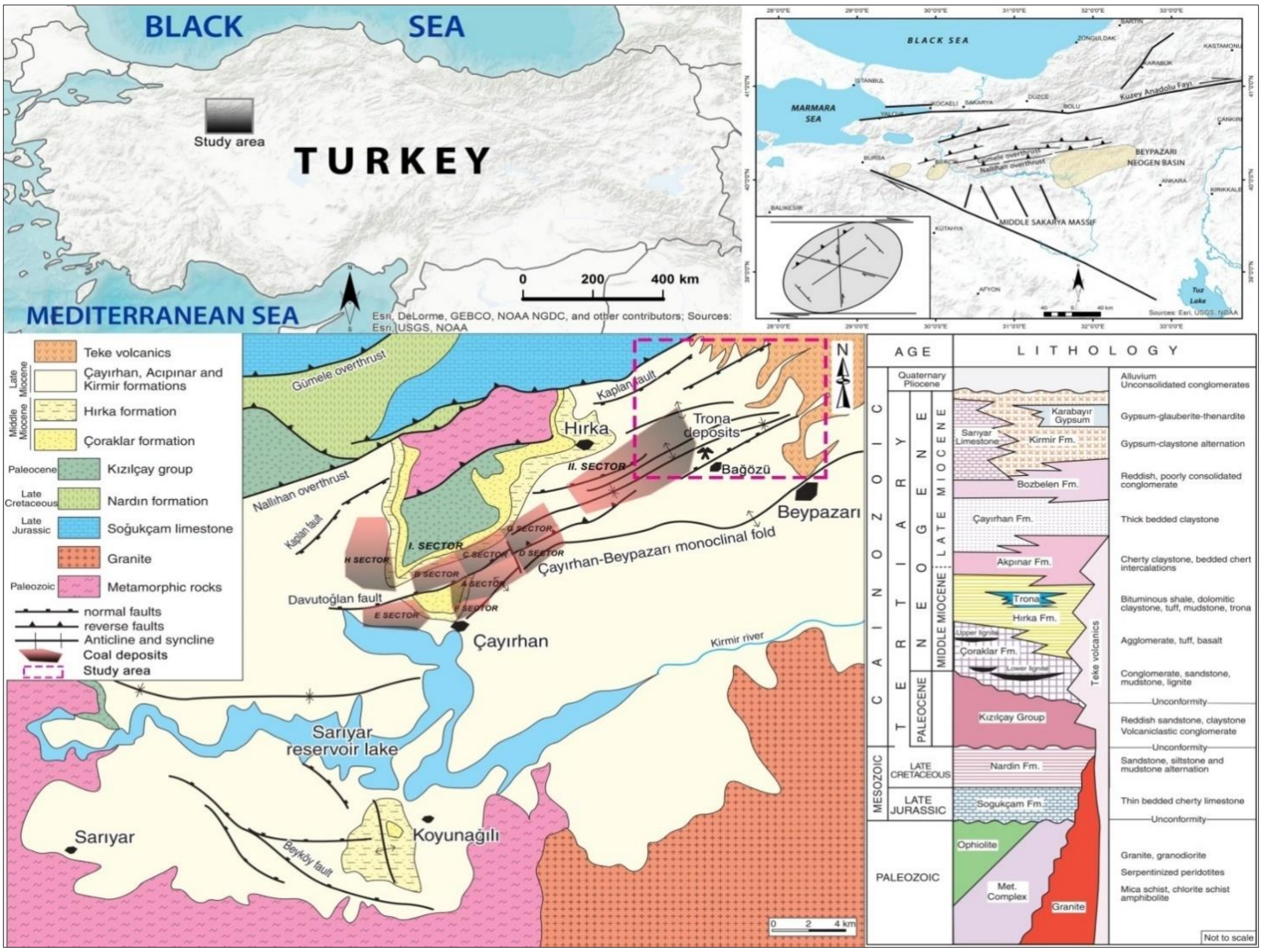

Figure 1. Geology and tectonic maps of the study area (modified from Yağmurlu et al., 1988a; Tarvirdi, 2013; Helvacı, 2018)

Oil shales in the Beypazarı Neogene Basin were formed within the Hırka Formation during the Miocene. Hırka Formation is a volcano-sedimentary sequence, reflecting the lacustrine environment conditions whose water level varies continuously (Yağmurlu et al., 1988c). Oil shales are in the form of small pockets (Ziegler, 1939). They are quite common in the basin and the thickness of the levels containing bituminous shale varies from 57 to 111 m (Gülbay, 2004; Vardaloğlu, 2016). Total organic carbon (TOC) values change in each location and average TOC values are concentrated between 4% and 8% (Gülbay, 2004). Algal organic matter (kerogen) is dominant and featured by Type I-II. According to vitrinite reflection values and T_{max} values, the organic matter has not reached a sufficient maturity and not yet entered the oil window (Özçelik, 2002; Gülbay, 2004; Özçelik and Altunsoy, 2005; Vardaloğlu, 2016). Bituminous shales have 83% pyrolysable hydrocarbon content. They are appropriate for oil generation and a potential source that can produce oil on a large scale if exposed to higher temperatures (Gülbay, 2004). It can be interpreted that it reflects a lacustrine environment with high anoxicity, a possibly salty and mostly algal, and very little amount of terrestrial organic matter input (Gülbay and Korkmaz, 2005). Trona deposits, which constitute the other significant economic potential of the region, are located in the lowest part of the Hırka Formation and an alternating structure with bituminous shales (Yağmurlu et al., 1988a).

The bituminous shales of Beypazarı Neogene Basin have the potential source rock characteristics that can produce oil on a large scale if they are exposed to high temperatures. Beypazarı Neogene Basin consists of volcano-sedimentary units. Therefore, in this study, based on the idea that the immature source rocks can be matured by young volcanics that present widespread outcrops, especially in the northeastern part of the basin, it has been aimed to investigate the oil and gas potential of the basin by TPH (Total Petroleum Hydrocarbons) analysis performed on the samples taken from the natural cold water resources located in the northeastern of the basin. As a result of the analyses conducted, hydrocarbons have been detected in all the water samples. The determined n-alkane hydrocarbons are the mature petroleum hydrocarbons derived from peat/coal type organic mater (Type III kerogen, gas-prone) and these mature petroleum hydrocarbons are evidence for the presence of a working petroleum system in the research area.

2. GEOLOGICAL SETTING

Neogene sediments of Beypazarı Neogene basin are Middle-Upper Miocene aged and their total thickness is around 1200 meters. Paleozoic and Eocene basement rocks are unconformably covered by these Miocene aged sediments which filled the basin (Figure 1). These units are deposited in alluvial and lacustrine environments and locally contain volcanoclastic intercalations. The Miocene units in the Beypazarı Neogene Basin are separated from each other by time-exceeding boundaries that can be laterally and vertically inclined, depending on the changing lithofacies conditions from west to east. Most of the Miocene units are covered by Teke volcanics towards the northeast of the basin. Çoraklar Formation consists of a fluvial origin and cross-layered conglomerate, sandstone, siltstone, mudstone, terrestrial limestone intercalations, and two lignite levels. The thickness of Çoraklar Formation, which unconformably overlays the older units, varies from 80 to 237 m. The Hırka Formation composes of thin laminated mudstone, claystone, oil shale, calcareous shale, dolomitic limestone, tuff, trona, and locally intraformational breccia. The Hırka Formation, which reaches a thickness of 300 m in the basin, has been deposited in a playa-type lacustrine environment according to the composition and lithological characteristics it reflects (Yağmurlu et al., 1988a; İnci, 1991; Helvacı, 2018) whereas Cenozoic formations reflect a very shallow and active environment in Paleocene-Lower Eocene and Oligocene. The environmental conditions, which became quite shallow from the beginning of Paleocene-Eocene to the end of Oligocene, have acquired a terrestrial character in Miocene. In the Lower Miocene, terrestrial flow and rash volcanics developed from time to time. Volcanic units, which are highly effective on the sedimentation of coal and other sedimentary rocks and outcropped with extensional tectonics as a result of the movement of the North Anatolian Fault (NAF) in Miocene, present a rather complex relationship with Neogene basin sediments laterally and vertically. Paleotopographic basement uplifts controlled by developed block faults in Miocene indicates the presence of a lacustrine environment that deepens from south to north, where the uplifts of the basement are common in the southern parts. The outcrops, which usually characterize the coastal and near-shore parts, indicate the presence of a lake deepening under the volcanic cover. It is believed that suitable conditions for organic rock deposition occur in these lake(s) where the volcanic ash debris changes with the wind directions and the pH of the environment is controlled in paleoclimatological and paleogeographic parameters (Toprak, 2010).

There are thrust faults, high-angle reverse faults, and normal faults in the Beypazarı Neogene Basin. These faults are generally E-NE trending and approximately parallel to each other. The strike-slip faults transversely cut these fault systems. The normal faults were generally developed as step faults approximately parallel to each other in the south and north of the basin. These faults behaved as growth faults during the collapse. In later periods, normal and/or growth faults transformed to reverse faults. The formation of normal and strike-slip faults, which transversely or obliquely cut normal and reverse faults, also occurred during this compression period (Figure 2). The products of this compressional tectonics, probably occurring at the end of Miocene, outcropped in the north of the basin. Therefore, the basement rocks are visible on the surface. The breccia conglomerates in the Hırka Formation indicate concurrent tectonism along with precipitation. In particular, the structural development of the northern part of the basin has been largely completed by extensional tectonics.

Asymmetric fold systems, monoclinal structures, and reverse fault systems indicate that the compressional tectonics gradually took the place of the extensional tectonics in the basin towards the end of Miocene. The structural features in the Beypazarı Miocene Basin are controlled by the North Anatolian and Eskişehir Faults. The opposite movement of the North Anatolian Fault to the Eskişehir Fault and the geostationary block of Central Sakarya Massive may have caused a one-way compressional regime that runs from north to south in the region (Yağmurlu et al., 1988b; İnci, 1991). This one-way compressional regime in the Miocene and pre-Miocene units in the study area has created numerous structures such as anticlines, synclines, recumbent folds, and fractured systems (i.e., Zaviye Fault, Koçali River Anticline, Beypazarı Monocline/Flexure) (Figure 1).

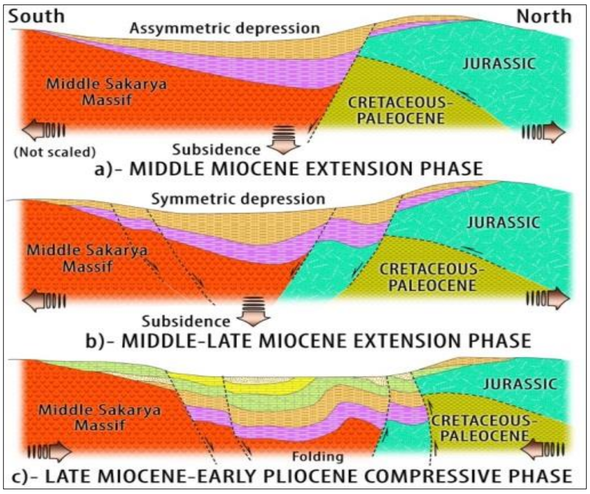

Figure 2. Tectonic development of Beypazarı Neogene basin (modified from Yağmurlu et al., 1988b; Helvacı, 2018)

3. MATERIAL AND METHOD

Eymold et al. (2018) 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. (2018) 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. 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) (Ozdemir, 2019a-c; Karataş et al., 2019; Palabiyik et al., 2019, 2020; Palabiyik and Ozdemir, 2020; Ozdemir et al., 2020). 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 3) (Ozdemir, 2018; Liu et al., 2018). 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 4). 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°C ± 3°C before the analysis.

In the comprehension of this research, totally 25 samples have been taken by the scaled polyethylene bottles of 1 liter from the natural flowing waters (cold water fountains) in the region (Figures 5 and 6). 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 utilized.

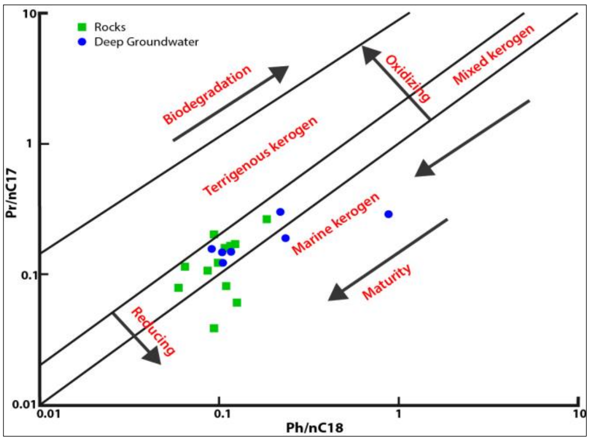

Figure 3. Ph/nC18 vs Pr/nC17 ratios of deep groundwater and rock samples taken from the same region (Liu et al., 2018) (Pr: Pristane and Ph: Phytane isoprenoid hydrocarbons, nC17 and nC18: n-alkane hydrocarbons)

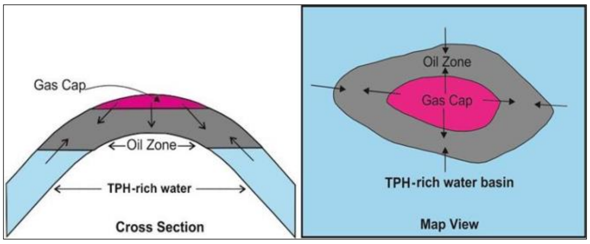

Figure 4. Components of an anticlinal type of petroleum reservoir that can be produced by primary methods (Ozdemir, 2018)

4. 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.

4.1. Contents, Source, and Biodegradation of Hydrocarbons in Waters

Liu et al. (2018) have defined groundwater of which hydrocarbon concentration exceeds 0.05 mg/l as original hydrocarbon-rich groundwater. The TPH limit values recommended for surface and subsurface waters are given in Table 1. Surface and subsurface waters exceeding the TPH values in Table 1 are defined as hydrocarbon-rich waters. The n-alkane hydrocarbons have been found in all the water samples in the study area. The hydrocarbon content of the water samples is much higher than the limit values suggested for the waters (Tables 1 and 2). Hence, it can be mentioned that water-rock-hydrocarbon interactions have created this hydrocarbon enrichment in waters.

Source, maturity, migration, and biodegradation are the main elements responsible for the compositional changes in hydrocarbons. Ph/n-C18 value less than 1 indicates non-biodegraded hydrocarbons (Hunt, 1995). Ph/n-C18 values of all the water samples are less than 1 and according to these values, the hydrocarbons in the water samples are in a non-biodegraded character.

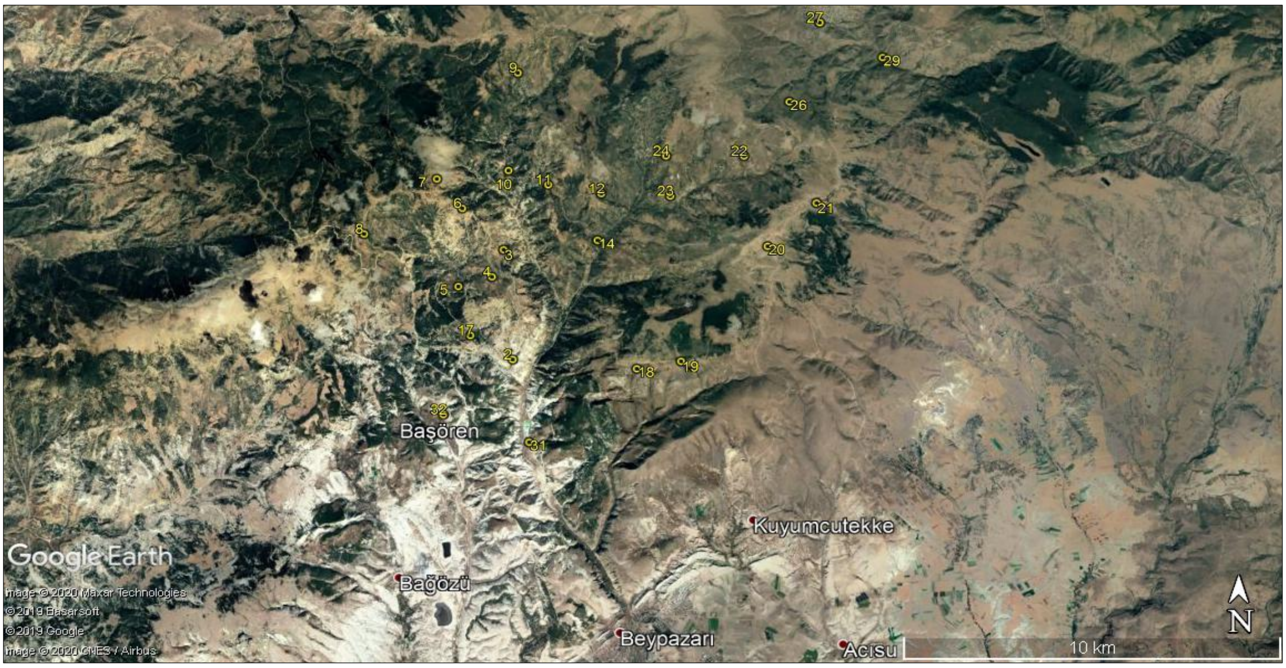

Figure 5. Location map of the taken water samples (yellow circles: the water samples)

Figure 6. A view of water sampling procedure from cold water fountains (pure and clean natural flowing waters) in the study area by using scaled polyethylene bottles

By making use of gas chromatography analysis outcomes, the Carbon Preference Index (CPI), Pr/Ph ratio, isoprenoid/n-alkane ratio (Pr/nC17 and Ph/nC18) have been computed, and the n-alkane distributions have been evaluated. In this study, Pr/Ph ratio (Didyk et al., 1978; Tissot and Welte, 1984; Banga et al., 2011), Carbon Preference Index (CPI) (Bray and Evans, 1961, 1965; Tissot and Welte, 1984), Pr/Ph versus CPI (Onojake et al., 2013; Hakimi et al., 2018), and Pr/n-C17 versus Pr/Ph (Syaifudin et al., 2015; Larasati et al., 2016; Devi et al., 2018) plots are utilized to assess the water samples. Organic geochemical parameters of bituminous shales in Beypazarı basin have been determined in some studies (Özçelik, 2002; Gülbay and Kormaz, 2005; Vardaloğlu, 2016). The results obtained from these studies are similar. Therefore, in this study, only the data in Vardaloğlu (2016)'s study are included in the plots.

Table 1. The TP limit values recommended for surface and subsurface waters

TPH (mg/l)	Reference
< 0.05	Liu et al. (2018)
< 0.1	Zemo and Foote (2003)
< 0.5	Ozdemir (2018)
< 0.2	Ministry of Agriculture and Forestry of Turkey (2004a), Surface Water Quality Regulation of Turkey (Appendix 5, Table 2: Oil and Grease)
< 0.02	Ministry of Agriculture and Forestry of Turkey (2004b), Water Pollution Control Regulation of Turkey (Appendices Table 1: Oil and Grease)

CPI is an indicator for the source of n-alkanes. The CPI, a ratio between the amounts of n-alkanes with odd and even carbon number, is calculated by measuring the heights of the peaks in gas chromatograms. The dominant peaks in these chromatograms are represented by n-alkanes. In the computation of the CPI, various equations have been proposed by numerous researchers. This index can be applied to any range of the carbon sequence. It is utilized to assess the kind of organic matter, the depositional environment, and thermal maturity. It is remarkably greater than 1 (odd n-alkane preferential) or lower than 1 (even n-alkane preferential), indicating thermally immature oil or bitumen samples (Tissot and Welte, 1984; Peters and Moldowan, 1993). A high value of CPI in the immature or low-maturity sample means the input of organic matter derived from higher terrestrial plants (Tran and Philippe, 1993). According to the CPI values (Table 2), the source of n-alkanes in the water samples remarks the petrogenic hydrocarbons and old organic-rich sediments (Table 3).

The term petrogenic sources describe unburned fossil resources like crude oil and coal. These types of sources were formed very slowly at moderate temperatures (between 100°C and 300°C) millions of years ago (Beyer et al., 2010). The parameter NAR (Natural n-alkane Ratio) has been suggested to interpret the source of hydrocarbons in the environment (natural or petroleum n-alkane). This ratio is zero or approximately zero for natural petroleum hydrocarbons and crude oil. In other hydrocarbon sources, those ratios are greater. According to the parameter NAR (Table 2), all the n-alkanes in the water samples indicate natural petroleum (petrogenic) hydrocarbons.

The parameter TAR (Terrestrial/aquatic hydrocarbon ratio) shows the ratio of n-alkanes derived from terrestrial organic matter to n-alkanes derived from aquatic algae (Cranwell et al., 1987; Goossens et al., 1989; Meyers and Ishiwatari, 1993; Bourbonniere and Meyers, 1996). High values of TAR (greater than 1) sign terrestrial plant source and its low values (less than 1) mean marine algae source (Kroon, 2011). The TAR values have been calculated as quite high for the inspected water samples (greater than 1) (Table 2). These values show that the n-alkanes having high carbon numbers indicating terrestrial organic matter are dominant in the water samples in the examined area.

Waxiness index can be utilized to determine the amount of terrestrial organic matter. This index depends on the assumption that regional terrestrial organic matter contributes to extracts with the n-alkane components with high molecular weight (Peters et al., 2005). It is observed that the water samples in the investigation area have high Waxiness values indicating high amounts of biomarkers derived from terrestrial plant (Table 2). This finding is also supported by the fact that the analyzed samples show high TAR values.

The n-C17/n-C31 ratio indicates the source of the hydrocarbons derived from the organic matter in the environment. High values (higher than 2) correspond to marine algae while low values (lower than 2) sign land plant sources (Forster et al., 2004). The ratio of n-C17/n-C31 of the water samples ranges from 0.11 to 0.26 by indicating the terrestrial organic matter. This consequence is consistent with TAR and Waxiness index values.

By calculating P_{aq} and P_{wax} parameters, some interpretations can be made about the plant species that make up the organic matter and the paleoclimate conditions of the environment (Zheng et al., 2007). These parameters are used only for coals. If P_{aq} value is less than 0.1, it will mean terrestrial plants; if it is between 0.1 and 0.4, it will refer to aquatic plants (floated in the swamp environment), and if it is between 0.4 and 1.0, it will mean that environments exist the presence of plants floated in the water (Ficken et al., 2000). According to P_{aq} values (Table 2), the types of plants that constitute the organic matter-deriving hydrocarbons in the water samples are predominantly aquatic plants (floated in the swampy environment). If the P_{wax} value is lower than 0.7, it means dry climate conditions whereas if it is less than 0.7, it will mean the existence of humid climate conditions (Zheng et al., 2007). According to the P_{wax} values (Table 2), the organic matter-deriving hydrocarbons in the water samples was formed in dry climate conditions.

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

Sample No.	Water Resource	Coordinates		TPH (mg/l)	CPI	TAR	NAR	n-C17/n-C31	P_{aq}	P_{wax}	Waxiness Index	Pr/Ph	Pr/n-C17	Ph/n-C18
		X	Y											
2	Natural flowing water	4454774	405296	0.62	1.61	11.78	0.06	0.12	0.07	0.93	2.58	6.87	0.31	0.11
3	Natural flowing water	4457891	405075	0.59	1.60	7.85	-	0.19	-	-	5.37	9.56	0.25	0.08
4	Natural flowing water	4457124	404758	0.46	1.59	7.10	0.03	0.26	0.18	0.82	3.43	7.93	0.25	0.09
5	Natural flowing water	4456858	403857	1.00	1.61	7.92	0.09	0.17	0.06	0.94	2.17	6.29	0.25	0.12
6	Natural flowing water	4459077	403980	0.47	1.52	9.63	0.11	0.16	0.06	0.94	2.72	12.18	0.29	0.06
7	Natural flowing water	4459918	403305	0.71	1.57	8.69	-	0.14	-	-	2.27	7.40	0.30	0.09
8	Natural flowing water	4458370	401349	0.68	1.62	8.26	0.02	0.17	0.11	0.89	2.64	8.91	0.28	0.09
9	Natural flowing water	4462912	405492	0.59	1.62	8.22	-	0.14	-	-	2.28	10.77	0.28	0.07
10	Natural flowing water	4460140	405221	0.52	1.62	7.98	-	0.15	-	-	2.28	17.17	0.30	0.06
11	Natural flowing water	4459726	406279	0.65	1.60	7.58	0.10	0.18	0.10	0.90	3.83	8.44	0.24	0.08
12	Natural flowing water	4459462	407693	0.53	1.61	7.56	-	0.19	-	-	4.26	13.04	0.29	0.06
14	Natural flowing water	4458137	407582	0.57	1.67	7.55	0.11	0.17	0.08	0.92	3.71	5.14	0.06	0.04
17	Natural flowing water	4455466	404170	0.58	1.57	-	0.10	0.11	0.17	0.83	-	6.40	0.33	0.11
18	Natural flowing water	4454486	408601	0.57	1.59	-	0.18	0.13	0.17	0.83	-	7.22	0.36	0.12
19	Natural flowing water	4454688	409785	0.47	1.61	7.61	0.20	0.19	0.17	0.83	6.12	9.45	0.27	0.08
20	Natural flowing water	4457929	412115	0.55	1.65	-	0.27	0.16	0.24	0.76	-	7.62	0.26	0.09
21	Natural flowing water	4459147	413428	0.64	1.67	-	0.27	0.15	0.20	0.80	-	7.87	0.31	0.11
22	Natural flowing water	4460495	411507	0.66	1.67	6.61	0.27	0.20	0.17	0.83	5.02	7.37	0.25	0.12
23	Natural flowing water	4459378	409534	0.60	1.64	6.67	0.32	0.19	0.20	0.80	5.13	6.78	0.25	0.14
24	Natural flowing water	4460520	409429	0.75	1.67	6.28	0.25	0.20	0.10	0.90	4.57	6.95	0.21	0.10
26	Natural flowing water	4462023	412729	0.43	1.63	8.17	0.24	0.17	0.16	0.84	6.13	7.00	0.32	0.13
27	Natural flowing water	4464265	413558	0.56	1.67	7.35	0.18	0.19	0.11	0.89	5.58	9.49	0.27	0.08
29	Natural flowing water	4463259	415222	0.57	1.60	8.72	0.05	0.13	0.09	0.91	2.21	14.38	0.27	0.05
31	Mineral water	4452425	405715	0.69	1.71	6.94	0.23	0.18	0.10	0.90	5.00	10.51	0.23	0.07
32	Natural flowing water	4453224	403432	0.63	1.61	6.54	0.23	0.20	0.14	0.86	4.68	11.69	0.23	0.07

CPI = {[(C23+C25+C27) + (C25+C27+C29)] / [2 *(C24+C26+C28)]} (Bray and Evans, 1961), TAR = (C27+C29+C31)/(C15+C17+C19) (Bourbonniere and Meyers, 1996), NAR = [Σn-alk (C_{19-32}) - 2Σ even n-alk (C_{20-32})] / Σ n-alk (C_{19-32}) (Mille et al., 2007), Waxiness Index:∑ (n-C21-n-C31)/∑ (n-C15-n-C20) (Peters et al., 2005), P_{aq} = (C23+C25)/(C23+C25+C27+C29+C31) (Ficken et al., 2000), P_{wax} = (C27+C29+C31)/(C23+C25+C27+C29+C31) (Zheng et al., 2007), - : Could not be calculated.

Table 3. Source of n-alkanes in water according to CPI value (Ozdemir, 2018)

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

4.2. Maturity of Hydrocarbons in Waters and Redox Conditions of Sedimentation Environment

CPI value of mature hydrocarbons is equal to 1 or close to 1 (Waples, 1985). The CPI values of oil and bitumen related to very salty carbonate or evaporitic environments are lower than 1 (Tissot and Welte, 1984; Peters and Moldowan, 1993). The maturity level of hydrocarbons is classified based on their CPI values (Table 4) (Onojake et al., 2013), and depending on this classification, all the hydrocarbons in the water samples (Table 2) can be classified as mature (more oxidizing) level.

Table 4. The maturity level of hydrocarbons according to CPI value (from Onojake et al., 2013) (see Figure 7)

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

The n-alkanes, which are the closest to isoprenoids in gas chromatograms, are utilized for isoprenoid/n-alkane ratios. The Pr/Ph ratio is an appropriate correlation parameter. Even though pristane (Pr) and phytane (Ph) define other sources, they are derived from phytyl, which is the side chain of chlorophyll, particularly 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 (Peters and Moldowan, 1993). Hence, the Pr/Ph ratio shows the redox potential of the depositional environment. Pr/Ph values lower than 1 reflect anoxic conditions while the values higher than 1 remark oxic conditions (Didyk et al., 1978; Hunt, 1995). The water samples in the study area exhibit a high Pr/Ph ratio varying from 5.14 to 17.17 (Table 2). Therefore, the water samples contain the hydrocarbons derived from sediments deposited in an oxic environment (Pr/Ph > 1). The Pr/Ph ratio also provides information about paleoenvironment and maturity (Volkman and Maxwell, 1986) level. In the Pr/Ph versus CPI relationship, it can be observed that the hydrocarbons in the water samples are located in the more oxidizing zone and have similar maturity levels (Figure 7).

Pr/n-C17 and Ph/nC18 ratios are commonly made use of in petroleum correlation studies. Samples containing high Pr reflect an oxidizing source, and high Ph content indicates a reducing source. Thus, the plot of Pr/n-C17 versus Ph/n-C18 is utilized to distinguish petroleum or bitumen in different groups (Hunt, 1995). Although the Pr/Ph ratio above 1.5 shows settling conditions in an oxygenated environment based on a standard geochemical interpretation, it is well-known that it may be lower than 1 for an anoxic depositional environment. Lower values may indicate less suitable oxic conditions than the other parts of the same sequence (Hartkopf-Fröder et al., 2007). The ratio of isoprenoid/n-alkane decreases with increasing maturity as more amounts of n-alkanes release from kerogen affected by a breaking down process (Tissot and Welte, 1984; Hunt, 1995) and is used as a degree of maturity for biodegradable oil and bitumen samples. It increases with the biodegradation (Hunt, 1995) and is also affected by organic matter input and secondary phenomena. Depending on their positions in the Pr/nC17 versus Ph/nC18 plot of the water samples, it is observed that the source rocks which generated the hydrocarbons in the water samples are deposited in oxic terrestrial (Type III kerogen, gas-prone) environment and exhibit a high maturity (Figures 7-11 and Table 5). Even though oxic paleo-environment conditions is generally probable for Çoraklar ve Hırka Formations, it has been concluded that anoxic and suboxic paleo-environment conditions is also possible (Sönmez, 2016). To sum up, it is revealed that the results obtained from this study are compatible with those of Sönmez (2016)'s study.

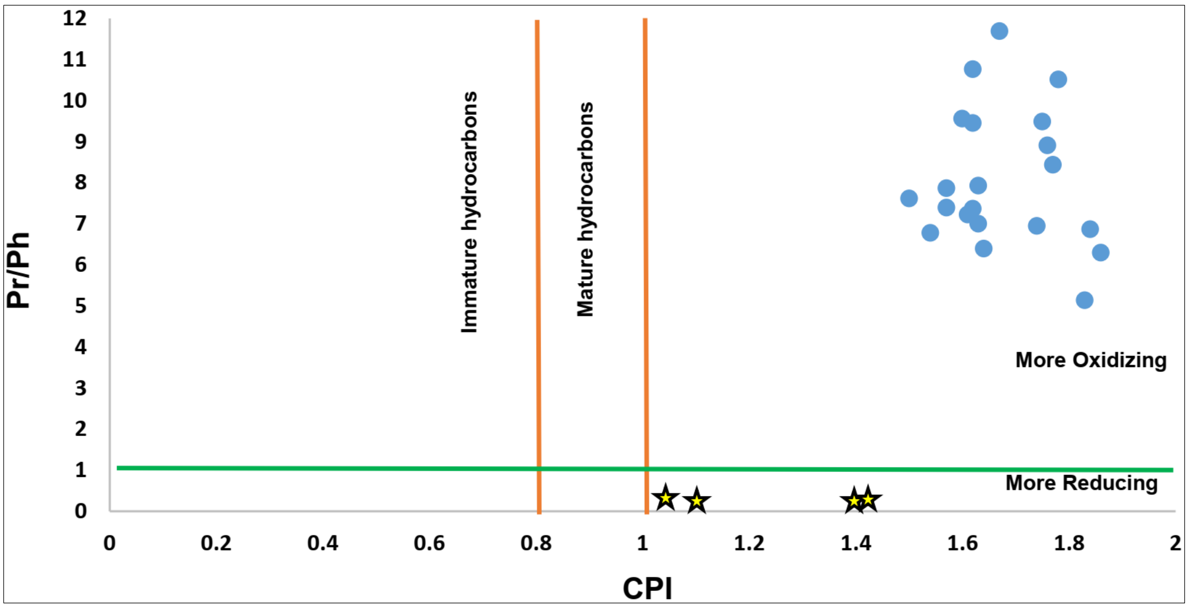

Figure 7. Pr/n-C17 vs Ph/n-C18 plot (the plot: from Peters et al., 1999). Blue circles: the water samples (this study), yellow stars: the samples of Beypazarı bituminous shale (the data: Vardaloğlu, 2016)

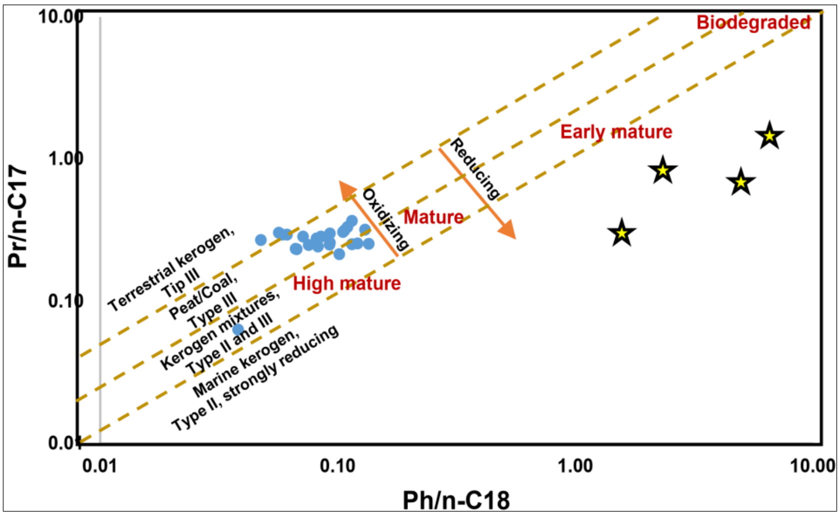

Figure 8. Pr/n-C17 vs Ph/n-C18 plot of the water samples (the plot: from Peters et al., 1999). Blue circles: the water samples (this study), yellow stars: the samples of Beypazarı bituminous shale (the data: Vardaloğlu, 2016)

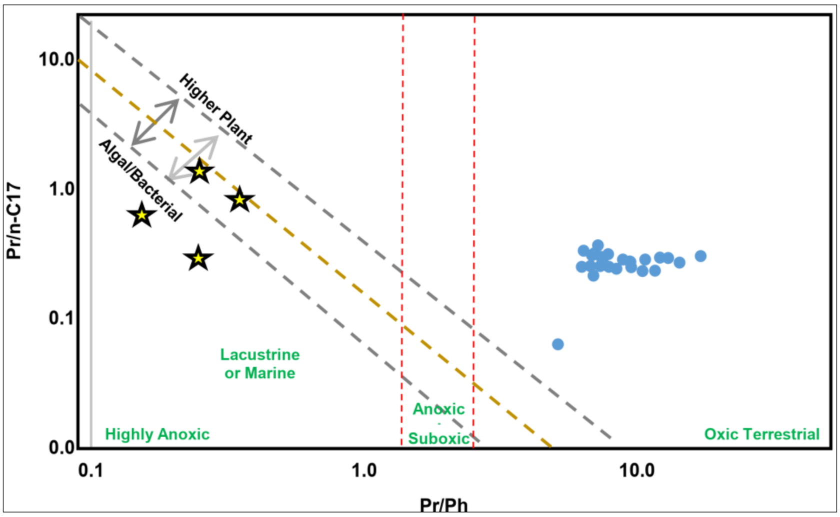

Figure 9. Pr/n-C17 vs Pr/Ph plot of the water samples (the plot: from Devi et al., 2018; Larasati et al., 2016; Syaifudin et al., 2015). Blue circles: the water samples (this study), yellow stars: the samples of Beypazarı bituminous shale (the data: Vardaloğlu, 2016)

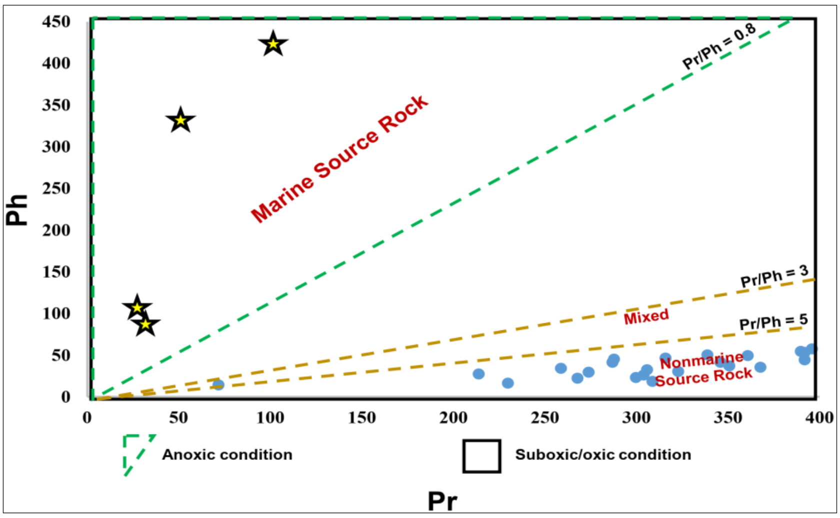

Figure 10. Ph vs Pr plot of the water samples (the plot: from Banga et al., 2011). Blue circles: the water samples (this study), yellow stars: the samples of Beypazarı bituminous shale (the data: Vardaloğlu, 2016)

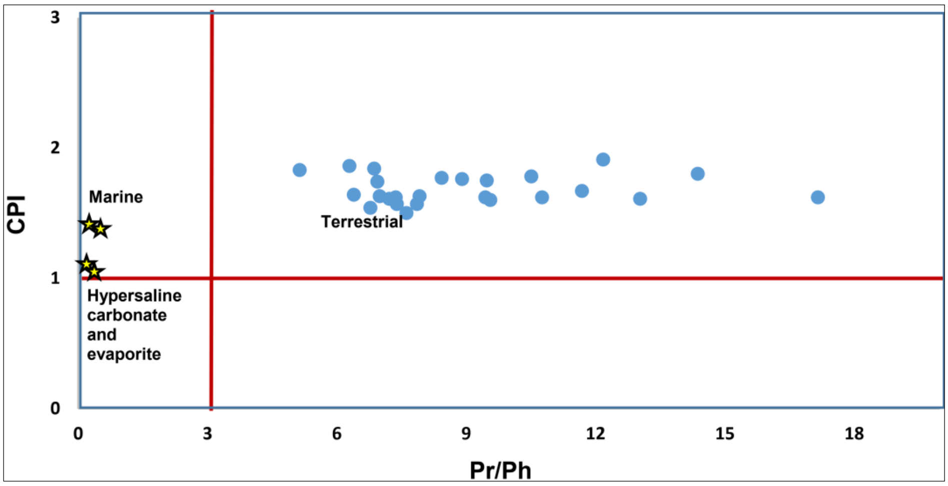

Figure 11. Pr/Ph vs CPI plot of the water samples (the plot: from Hakimi et al., 2018). Blue circles: the water samples (this study), yellow stars: the samples of Beypazarı bituminous shale (the data: Vardaloğlu, 2016)

Table 5. Source rock and depositional environment of hydrocarbons according to Pr/Ph value (from Banga et al., 2011) (see Figure 10)

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

4.3. Aeromagnetic and Gravity Maps of the Study Area and Geological Interpretations

There are a lot of studies regarding the methods and field applications of gravity and aeromagnetic data for use in oil and gas exploration (Griffin, 1949; Nettleton, 1976; Geist et al., 1987; Lyatsky et al., 1992; Gadirov, 1994; Piskarev and Tchernyshev, 1997; Pašteka, 2000; Aydın, 1997, 2004; Gadirov and Eppelbaum, 2012; Ivakhnenko et al., 2015; Satyana, 2015; Eke and Okeke, 2016; Stephen and Iduma, 2018; Gadirov et al., 2018; Ozdemir, 2019a-c; Ozdemir et al., 2020). Analysis of gravity and magnetic anomalies has been a permanent component of hydrocarbon exploration and discovery in West Siberia for half a century (Piskarev and Tchernyshev, 1997). In the regions where the existence of mature petroleum hydrocarbons is proved by the determination of hydrocarbon-rich waters in this research, particularly seismic surveys are crucial to determine the locations of oil and gas reservoir(s)/trap(s). Unfortunately, no seismic lines/measurements are available in the investigated area. The contour maps specifically prepared for the study area from regional gravity and aeromagnetic data measured by the General Directorate of Mineral Research and Exploration of Turkey (MTA) have been utilized to evaluate subsurface geology of the area.

The gravity map prepared for the study area (Figure 12) 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 characterized by the rocks having relatively higher densities (crystallized limestone, marble, quartzite, schist, etc.).

The prepared aeromagnetic map for the study area (Figure 12) demonstrates the anomalies that originated from fully non-magnetic sedimentary (sandstone, limestone, siltstone, mudstone, claystone, conglomerate, shale, etc.) and metamorphic (crystallized limestone, marble, quartzite, schist, etc.) rocks represented by blue, green, and light green colors. In the areas represented by yellow, red, and white tones, there are the rocks with magnetic properties (pebbly volcanic sandstones, ophiolites, dikes, etc.). Hydrocarbon reservoirs are located mostly at the slopes of both positive gravity and magnetic anomalies (in areas where both gravity and magnetic anomaly are high) in Northwestern Siberia. All known oil and gas deposits are in regions characterized by relatively high gravity anomalies (Piskarev and Tchernyshev, 1997). In the magnetic and gravity maps of the study area, the structures located in the areas where both gravity and magnetic anomalies are positive together are potential gas reservoirs. Tectonic structures in and around the study area were investigated by İnci (1991) and Seyitoğlu et al. (2017). Seyitoğlu et al. (2017) stated that there are many blind thrust faults in the study area. According to the gravity map, the potential gas traps are located between these blind thrust zones (Figure 12).

In the study, the interpretation method proposed by Svancara (1983) and Töpfer (1977) is used to convert the 2D (two-dimensional) residual gravity anomalies into the depth values for the estimation of the basin and structure depths. In this method, if the density contrast is known, the depth of the sedimentary basin or structure can be determined by simple relations established between gravity anomaly and parameters. The first stage of the interpretation gives the characteristic parameters of the anomaly (Figure 13). The relevant equations can be expressed as follows:

$$A = \frac{g_{mak}}{W_a \sigma} \quad (1)$$

Where

g_{mak}: Maximum amplitude of the gravity anomaly,

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

σ: Density contrast.

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

$$D_o = 23.866 \frac{g_{mak}}{\sigma} \quad (3)$$

For the condition 0 < A < 9 (Töpfer 1977):

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

For the condition 9 < A < 13 (Töpfer 1977):

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

where

W_b: Full width of the gravity anomaly,

D_i: Depth corresponding to the gravity anomaly value,

D_o: Depth obtained from the flat-plate formula,

D: Maximum depth.

An A-B profile is obtained from the residual gravity anomaly map of the study area (Figure 12). According to the anomalies of residual gravity map of the study area, the maximum depth of the structure (D) has been calculated as 110 m (Figure 14). The depth of the computed potential traps well-matches with the data of Seyitoğlu et al. (2017).

The mature hydrocarbons-rich waters are evidence for a working petroleum system in the study area. Possible gas reservoirs in the study area are the blind thrust anticlines which is determined by the gravity and magnetic maps (Figures 11 and 13). The fact that to be between two thrust zones of the structures, reinforces the possibility of having accumulated of hydrocarbons in these structures. Hydrocarbons-rich waters that migrate from the source rocks and/or oil reservoirs in the subsurface cause definable changes in the hydrocarbon concentration of surface and subsurface waters (Özdemir, 2018). Hydrocarbons in the water samples are enriched as a result of the water-rock-hydrocarbon interaction with the hydrocarbon-rich geological units in the subsurface and/or mixed with shallow groundwaters migrated from the potential reservoirs determined by gravity and magnetic maps (Figure 12).

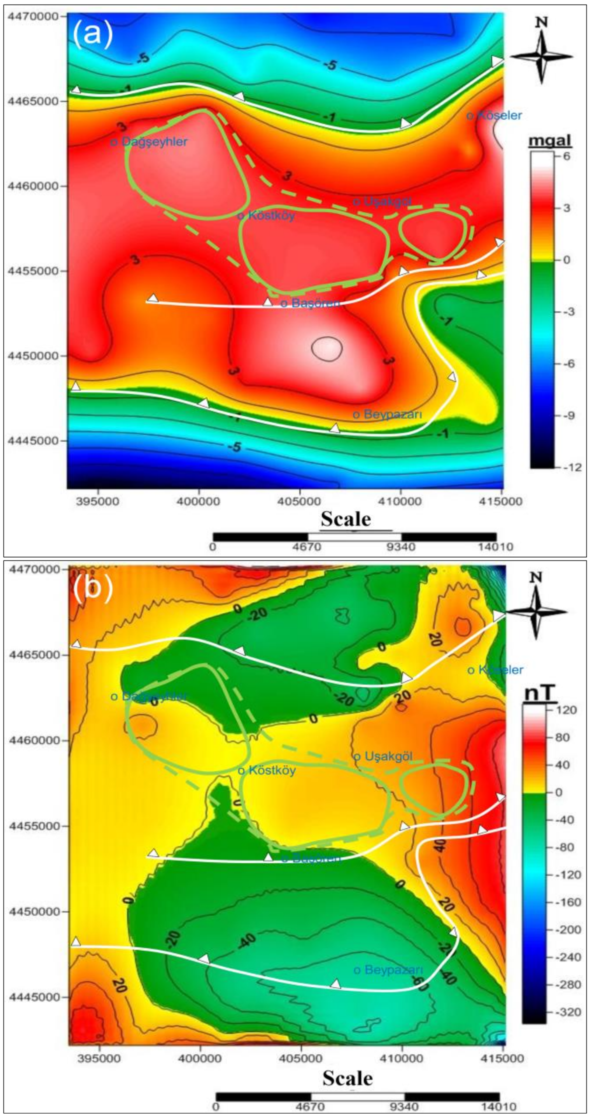

Figure 12. The colored contour maps and geological interpretations of the regional gravity (a) and aeromagnetic (b) anomalies of the study area. Green polygons: possible gas traps:, white lines: blind thrust faults (teeth show the overthrust unit)

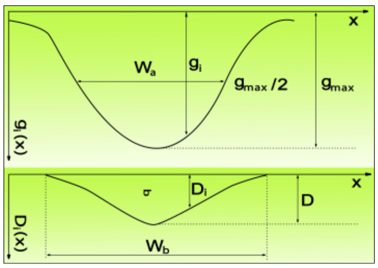

Figure 13. Ideal gravity anomaly of a basin and characteristic parameters (Svancara, 1983)

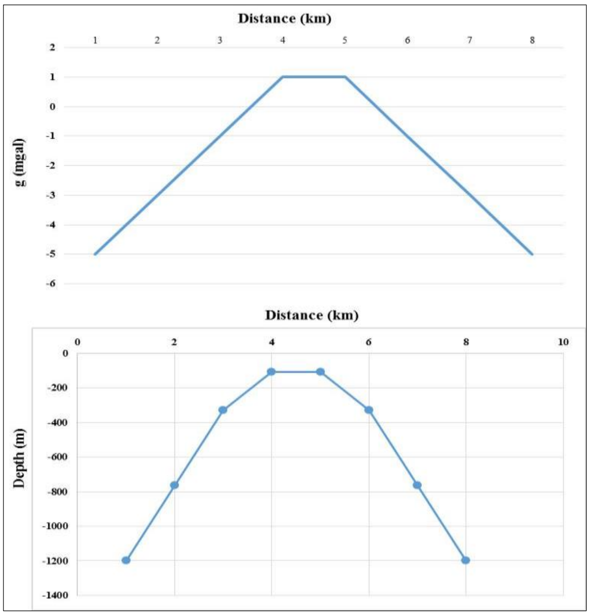

Figure 14. The depths of potential gas reservoirs in the study area

4.4. Conceptual Occurrence, Migration, and Trapping Model of Hydrocarbons in the Investigation Area

Ozdemir (2019a, b), Ozdemir and Palabiyik (2019a, b) and Ozdemir et al (2020) have mentioned that petroleum source rocks are formed in the mid-ocean ridges and the continental rifts (spreading centers). Hence, the source rocks which generated the hydrocarbons in the water samples should have formed in the geological periods that involved in the rifting process in the investigation area. In the area, the volcanism accompanying the expansion regime in the Early-Upper Miocene period should have brought about the occurrence of source rock in the region (Figures 2 and 15). Senger et al. (2017) have studied the impacts of magmatic intrusions on petroleum systems. The main elements of a petroleum system; (1) conditions leading to the hydrocarbon generation, (2) the ways in which hydrocarbons 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 elements of a petroleum system. Jointed and permeable magmatic intrusions can create new migration paths, or act as a fluid barrier when they are crystallized and impermeable (Senger et al., 2017). Hydrocarbon-rich waters can be transported from the hydrocarbon reservoirs to the surface and mixing with different origin waters (meteoric or sea waters, etc.) with the effect of these magmatic activities,. In the maturation process of the hydrocarbons in the water samples, it is considered that the emplacement of Beypazarı granite and intense volcanic activities are effective (Figure 1).

In the Late Miocene-Early Pliocene period (Fig. 2), many blind thrusts (Seyitoğlu et al., 2017) and fault-progression folds (Yağmurlu et al., 1988b; Helvacı, 2018) was formed in the basin due to the compression tectonics. Fault-propagation folds between blind thrusts are potential gas reservoirs (Figure 16). There are two different dolomite levels in the Hırka Formation, in the trona levels, and above and below trona levels (Özpeker et al., 1991). Consequently, the dolomites of Hırka formation and carbonate rocks in younger units in the identified structures are possible reservoir rocks.

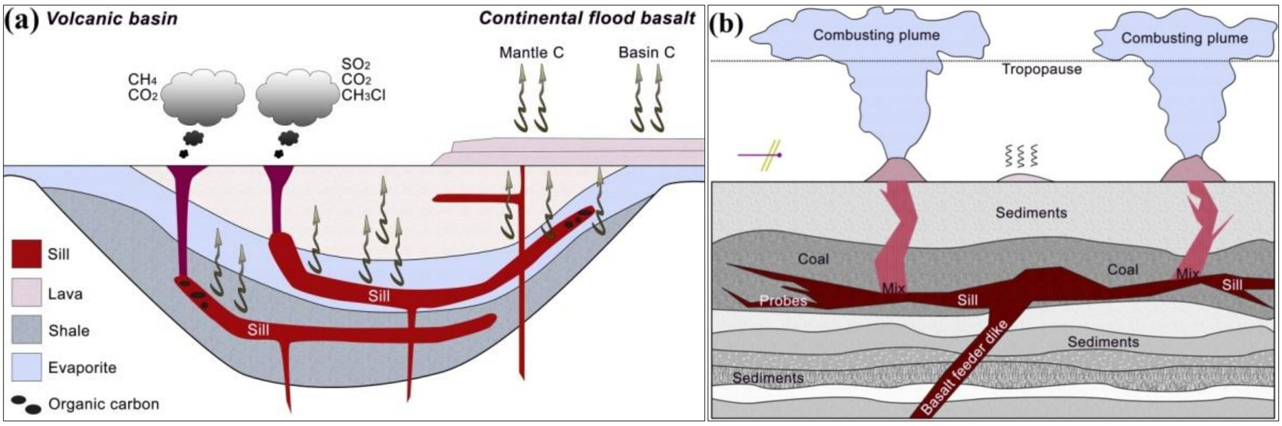

Figure 15. Schematic cross-section showing sil and dykes across a volcanic basin. The chemical composition of sedimentary rocks heated by igneous intrusions has a significant effect on the composition of the metamorphic fluid. For example, organic-rich shale produces CH_4 during contact metamorphism, while coal produces CO_2-derived fluids and also water. Many sedimentary basins with sil settlement may contain hydrogen-rich kerogen and oil and gas deposits, and fluids such as methane (CH_4) and ethane (C_2H_6) can be enriched in the basin (Svensen et al., 2015). (a: Svensen et al., 2015; b: Ogden and Sleep, 2011)

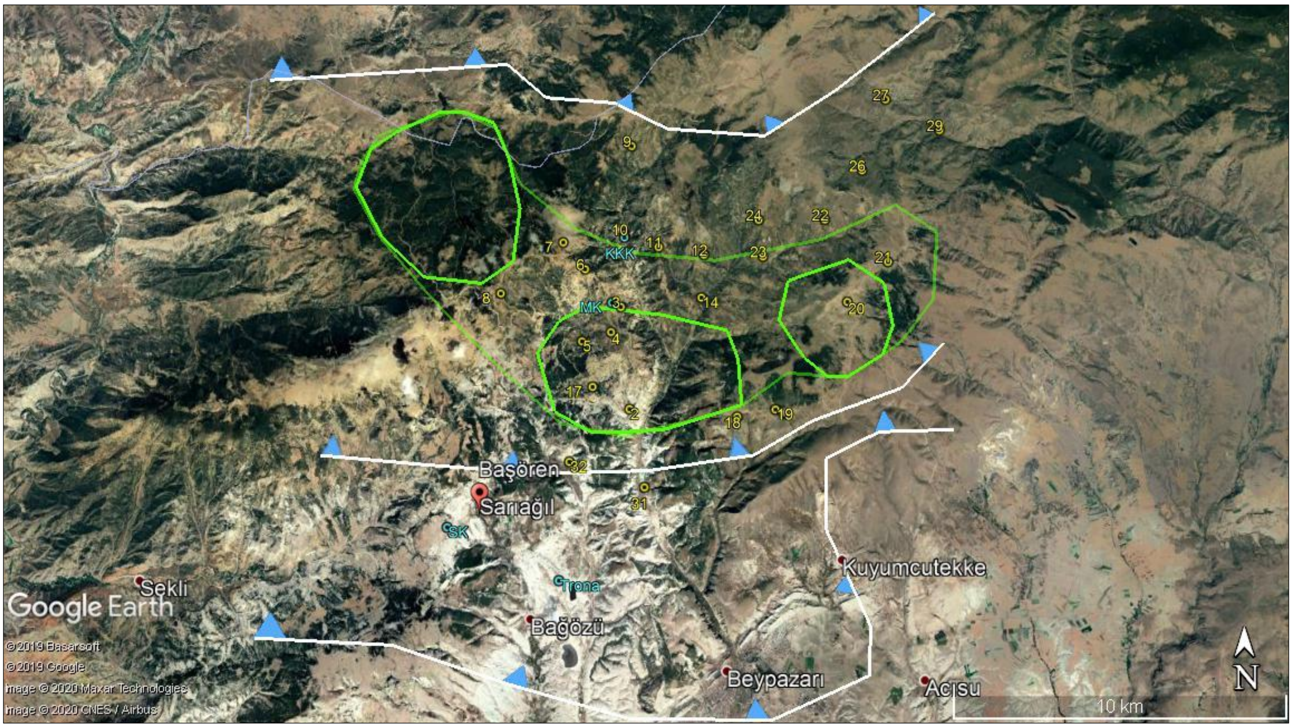

Figure 16. Possible gas traps in the study area (green polygons). Yellow circles: the water samples containing petroleum hydrocarbons, SK: Sarıağıl coal sector (Tarvirdi, 2013), KKK: Kabalar coal outcrop (Toprak, 2010), MK: Mençeler coal outcrop (Toprak, 2010), white lines: blind thrust faults (teethes are above the overthrust unit)

5. CONCLUSION

In this study, which is aimed to investigate the oil and gas potential of Beypazarı Neogene Basin using TPH analysis performed on the samples taken from water resources, the hydrocarbons have been determined in all the water samples based on the TPH analysis results. The TPH values are remarkably greater 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 sediments. Water-rock-hydrocarbon interactions have created a hydrocarbon enrichment in the waters in the examined area, and the hydrocarbons in the water samples are in a non-biodegraded character. It is come into existence that the source rocks which generated the hydrocarbons in the water samples were deposited in the oxic terrestrial environment (Type III kerogen, gas-prone) as well as corresponding to the mature-overmature level. In the magnetic and gravity maps of the investigation area, the anticlines in the fault-progression folds in the areas where both gravity and magnetic anomalies are positive are considered as potential gas reservoirs.

ACKNOWLEDGEMENT

We would like to thank Mr. Serkan Çelebi as well as the experts of SGS Supervise Gözetme Etüd Kontrol Servisleri A.S. for their precious performances to perform the required analyses to complete this research study.

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