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Geochemical Methods to Investigate the Hydrocarbon Seepage Samples in Adiyaman a Southeastern Province of Turkey

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ABSTRACT: The southeastern part of Turkey is quite rich, fertile and mature in terms of hydrocarbon seepages. While the use of the related sources meet the energy demand, it damages the environment and human health. In this study, several geochemical methods were applied to analyze the hydrocarbon sepage samples obtained from seven towns in the province of Adiyaman where is very close to the oil production areas and located in the Southeastern part of Turkey. First of all, Total Organic Carbon (TOC), Rock Evil Paralysis, Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry analyses (GC – MS) were performed for the samples in question. In the light of these results, oil/bitumen mechanisms, source rock correlations, formation and migration mechanisms of the related geological environments were found. Then, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis of Fe, Al, Mn, Mn, Zn, B, Pb, Ni, Cu metals were performed. Chemical and mineralogical features of the samples were investigated by IR and combined with ESR spectra. The samples display typical ESR spectra of Mn^{+2} ions hyperfine sextet whose last line was used to check the stones homogenity with respect to manganese content. In this study, heavy metal pollution and hydrocarbon compounds were determined to damage the environment and several suggestions were made to overcome the pollution and to enhance the productivity

Key words: Hydrocarbon seepage, Environmental Pollution, Metals, ESR, IR

INTRODUCTION

Being an expression of migration routes, hydrocarbon seepage is caused by underground oil flow through the reservoir source rocks (Clarke *et al.*, 1991). Hydrocarbon seepage comprises macro-leakages that are visible on the Earth's crust and micro-leakages that may be tracked by using different geochemical evaluation parameters (Meer *et al.*, 2002). Hydrocarbon seepages can be classified as natural and artificial. Although several studies related to the effects of artificial seepages to the environment have been conducted in the past, there hasn't been enough research on how natural seepages affect the environment and human health and necessary precautions haven't been taken. The geographical location of the hydrocarbon seepage carries a trail for its metal content, oil-oil and oil-rock correlation (Amorim *et al.*, 2007). Crude oil and bitumen which are present in hydrocarbon seepage contain several aromatic hydrocarbons, heteronuclear compounds, water and minerals. Metals are found in petroleum in organic and inorganic forms (Villares *et al.*, 2007). The most important parameters which determine the size of the damage that hydrocarbon seepage gives to the environment and human health are the heavy metals and aromatics having low boiling points.

The most important metals present in hydrocarbonseepage are vanadium (V), nickel (Ni), sodium (Na), potassium (K), lead (Pb), magnesium (Mg), iron (Fe), molybdenum (Mo), zinc (Zn), aluminum (Al) and manganese (Mn). Due to the fact that Adýyaman province and its environment located in the sotheastern part of Turkey are rich in terms of hydrocartbon seepages, several seepage samples were collected from the different towns in the region (Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar, Ýçmeler, Durukaynak) and their heavy metal concentrations were determined. After that, the heavy metal concentrations of those samples were

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*Corresponding author E-mail: htemelh@hotmail.com compared to the standard and permitted metal concentration values for water and soil in order to determine whether that cause environmental problems for Adiyaman province and the surrounding towns. If the dangerous effects of these metals inside the seepage were examined; air, water and soil contain different ranges of metal concentration (Swaine *et al.*, 2007). Earth metals such as Fe and Al show high level; Pb and Ni moderate level; B, Cu, Mn and Zn low level of toxicity. Metals cause important environmental, agricultural and health problems by accumulating in soil and plants (Table 1).

Being one of the most abundant elements in the earth's crust Fe, is the main component of soil, acts as a catalyst in photosynthesis and respiration in plants and is involved in the formation of sugars and starch. Iron also activates other enzymes. However, when the amount of Fe metal exceeds the limit value, it reduces the productivity of soil and the quality of the product obtained. Besides, it is toxic to the root of the plants (Fakih *et al.*, 2009). Aluminum is one of the most abundant eight element in earth's crust and is one of the main components of clay in soil. In basic or neutral pH values, Aluminum doesn't create a problem for plants. However, Al^{+3}, that is the soluble form of Aluminum in soil, is toxic to the root of the plants in acidic soils. When it is examined, manganese metal can be seen in different oxidation states such as +2, +3, +4 and sometimes +5. The steady state of manganese is its divalent cation. Mn +2 cation is important since it gives the ESR signal. The electronic configuration of Mn^{+2} ion, ends with $3d^5$ and its free ion ground state is ^6S. A distinctive feature of S-state ions such as Mn^{+2} is that they can give easily observable ESR signals at room temperature due to their long –lived electron spin states. Considering the above-mentioned harmful effects of the heavy metals within those seepages, experimental studies and observations performed at the settlement areas showed that due to these heavy metals, color of the plants turn to yellow and the soil was observed to reduce the expected yield because of the change in its physical properties. Additionally, the hydrocarbon seepage mixed with the soil structure is known to contaminate underground water

MATERIALS & METHODS

In the first stage of the study performed with seven hydrocarbon seepage samples collected from the settlements around the province of Adýyaman (Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar, Ýçmeler, Durukaynak), a literature search was done in order to determine whether if there were similar or different previous studies. Secondly, the samples were collected on a suitable day when the wheather temperature was around 30^0C and the soil around the seepage was observed whether dry or wet. This information let us know if the seepage was solid or liquid. Our samples were solid as their surrounding were dry. In order to examine the amount, type and the maturity level of the organic matter, these solid samples were analyzed by Total Organic Carbon (TOC), Rock–Eval Pyrolysis, Gas Chromatography (GC-FID), Gas Chromatography Mass Spectrometry (GC-MS). To determine the heavy metal concentrations ICP-OES, to characterize the aromatic structure and metal contamination Infrared Spectroscopy (IR) and Electron Spin Resonance (ESR) analyses were performed.

TOC analyses were performed by a LECO-Wr-12 instrument in Tubitak Scientific Research Laboratory. The core samples were powdered and treated with HCl. They were burned in the furnace of the instrument at the temperature range 700-1600 ^{o}C for 70 seconds. The emitted CO_2 gas was passed through the detector that was calibrated by a Standard having a known amount of carbon. Finally, the percent carbon in1 gr of sample was determined directly with a digital voltmeter. The rock-eval pyrolysis analysis was performed by using ROCK-EVAL VI instrument at TUBITAK Research Laboratories. Firstly, 100 mg of grounded sample was heated to 550 ^{o}C under anaerobic helium atmosphere. Hydrocarbons were formed at both 90 ^{o}C by giving S1 peak and 300-350 ^{o}C by giving S2 peak. Then, Hydrocarbons were detected by Flame Ionization Detector. The maturity level of kerogen was determined by looking at T_{max}(maximum point of S2 peak). Additionally, TOC amount of the rock was detected by measuring the resulting CO_2 gas by heat conductivity detector.

Table 1. Ecological Classification of significant metals (Burgos *et al.*, 2008)

Element	Requirement for Plant and Animal	Loss for plants and animals	Loss for Human Health	Pollutant or not
Cu	+	+	+	+
Fe	+	+	+	+
Mn	+	+	+	-
Pb	-	+	+	+
Ni	+	+	+	+
Zn	+	+	+	+
Al	-	+	+	+

GC analyses were performed by Shimadzu GC-17 model instrument after extraction of samples by ASE 300 Accelerated Solvent extraction system at Tubitak Research Laboratories. Prepared samples were loaded to the instrument by an injector. By applying a temperature program the seperation was achieved due to the differences in boiling points of the molecules. The seperated compounds were analysed by detector and their gas chromatograms were obtained.

GC-MS analyses were performed by Micromass Platform II mass spectrometry instrument coupled to an Agilent 6890 model gas chromatograph at Tubitak Research Laboratories. Prepared samples were introduced to the column of the gas chromatograph via an injector. The sample components were separated in a capillary column. Seperated components were then introduced to the ion source of the mass spectrometer. Here, they were bombarded by an applied electron beam and ions were generated. After the ionization ions were introduced to the mass analyser. Ions were seperated according to their m/z values and counted by an electron multiplier detector. These information came to the computer as electronic signals and ion chromataograms were obtained.

The ICP-OES analyses were performed by Perkin Elmer OPTIMA 3300 DV model instrument at TPOA. Seven solid samples were grounded and 0,5 grams of each were used for the analysis. 9 mL HNO_3 and 3 mL HCI were mixed with the solid samples. The mixtures were then extracted by a microwave oven. After sample preperation the liquified samples were analysed by the instrument. Obtained data were evaluated by a plotted calibration curve.

The IR analyses were performed by a Perkin Elmer Spectrum 100 model FTIR Spectrophotometer at Education Faculty of Dicle University. Seven solid samples were grounded and 0,1 grams of each were used for the analysis.

Electron spin resonance spectroscopy has been used for many applications since 1944. The use of ESR spectroscopy is based upon the existence of some paramagnetic centers in sample such as transitions elements ions or free radicals. Among the first category of paramagnetic centers, Mn^{+2} has been widely investigated in natural stones. In this part of the study we present the experimental results concerning the ESR spectra of Mn^{+2} in natural stones in connection with other analytical data. At the same time, the characteristic ESR spectra of Mn^{+2} ions in natural stones, consisting of six hyperfine structure line, each of them split into two fine structure doublet (Fig 2). Solid samples were powdered for the ESR

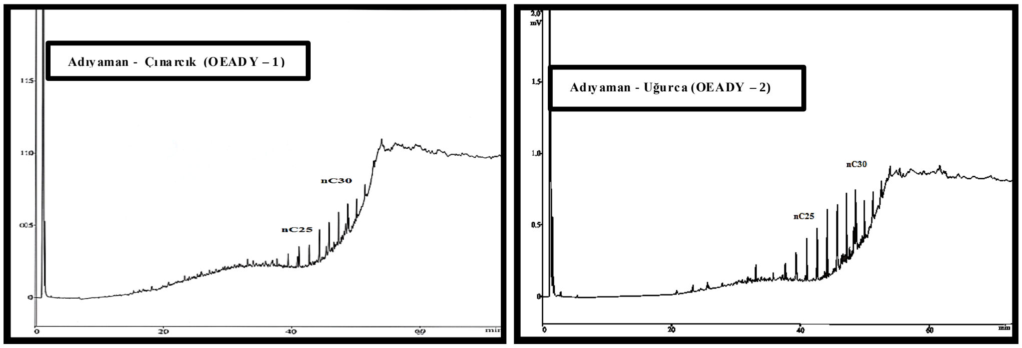

Fig. 1. GC chromatograms of Adýyaman – Çýnarcýk and Adýyaman – Uðurca

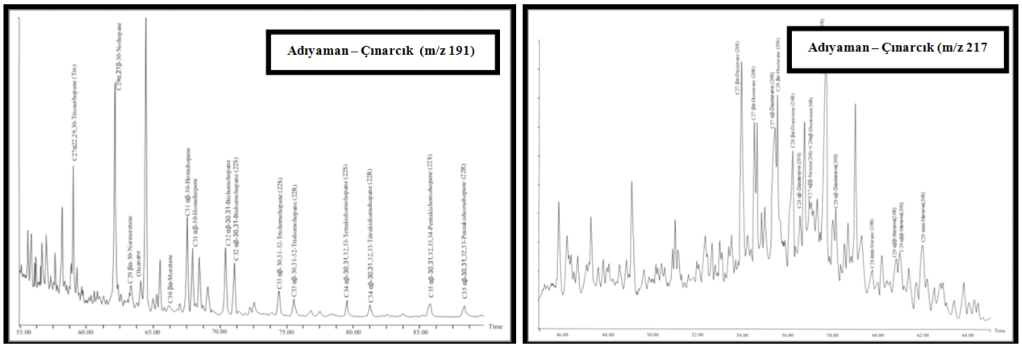

Fig. 2. Adýyaman – Çýnarcýk m/z 191-217 GC-MS chromotogram

measurements; the samples were introduced in quartz tubes with internal and external dia meters of 4.75 and 5.75 mm, respectively. The spectra were recorded with a Bruker EMX081 model EPR spectrometer using 2 mW micro wave power. The g values were calculated by comparison with a dipen hylpicryl hydrazyl sample of g = 2.0036.

RESULTS & DISCUSSION

The results of Total Organic Carbon (TOC), Rock Eval Pyrolysis, Gas Chromatography (GC), Gas Chromatography-Mass Spectrometry (GC-MS), Inductively Coupled Plasma Optical Emission Spctroscopy (ICP-OES), Infrared Spectroscopy (IR) and Electron Spin Resonance (ESR) analyses performed for Adiyaman Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar, Ýçmeler, Durukaynak samples were discussed below respectively. When the hydrocarbon seepage samples obtained from Adýyaman – Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar were examined, their % TOC values were higher than 2 which indicate very good source rock formation potential (Table 2). The hydrocarbon seepage sample from Adýyaman – Ýçmeler had TOC % value between 1 and 2 indicating good source rock formation potential. (TOC % value defines source rock formation potential) (Table 2, Table 3, Villares *et al*., 2007; Peters *et al*., 1993). The S1 values of Adýyaman – Çýnarcýk, Narlýk, Aliþar samples were over 2 and the amount of genetic potential that can be converted into hydrocarbons was very good. Additionally, in Uðurca and Ýzollu samples the S1 values were between 1 and 2 and the amount of genetic potential that can be converted into hydrocarbons was good. However, since the S1 values of Ýçmeler sample were smaller than 1 the amount of genetic potential that can be converted into hydrocarbons was medum (The S1 values define the amount of genetic potential that can be converted into hydrocarbons) (Table 2, Table 3, Villares *et al*., 2007; Peters *et al*., 1993; Tissot *et al*., 1984). The S2 values of Adýyaman – Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar samples were over 10 and of Ýçmeler sample was between 5 and 10 indicating thatthe amount of hydrocarbons formed by the breakdown of kerogen was very good in former samples and good in Ýçmeler sample (The S2 values define the amount of hydrocarbons formed by the breakdown of kerogen) (Table 2, Table 3, Peters *et al*., 1993). In the hydrocarbon seepage samples of Adýyaman – Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar, Ýçmeler, the HI values were over 300 which indicate that the hydrocarbons were of petroleum origin (The S2 values define geochemical parameters that identify the type of hydrocarbons) (Table 2, Table 4, Peters *et al*., 1993).

Table 2. TOC /Rock-Eval pyrolysis analysis results of the leak samples

Row No	Provincial	Sample Name	Sample Code	TOC %	S1	S2	S3	H1	O1	P1	Tmax
					(mg HC /g TOC)						
1	Adıyaman	Çınarcık	OEADY1	4.3	9.5	27.4	0.1	640	1	0.25	433
2	Adıyaman	Uğurca	OEADY2	5.7	1.1	32.8	1.2	572	21.5	0.03	428
3	Adıyaman	Narlık	OEADY3	68.6	70.2	493	1.7	719	2.5	0.12	434
4	Adıyaman	İzollu	OEADY4	5.5	1.0	33.9	0.8	613	14	0.02	432
5	Adıyaman	Alişar	OEADY5	2.7	7.1	16.1	0	602	0	0.30	430
6	Adıyaman	İçmeler	OEADY6	1.5	0.7	7.6	0.1	532	3	0.08	425

Table 3. The parameters defining the potential of the source rock formation (Peters *et al.*, 1993)

Amount	TOC (%)	S1	S2
Weak	0-0.5	0-0.5	0-2,5
Medium	0,5-1	0.5-1	2.5-5
Good	1-2	1-2	5-10
Very good	>2	>2	>10

Table 4. Geochemical parametersidentifying the type of hydrocarbons (Peters *et al.*, 1993)

Type	HI	S2/S3
Gas	0–150	0-3
Gas and Petroleum	150–300	3-5
Petroleum	>300	>5

Table 5. Tmax values represent the values of maturation

T_{max} (°C)	Maturity Rating
<435	İmmature
435 – 445	Early-Middle Mature
445 – 460	Intermediate – Advanced Mature
>460	Extreme Mature

Table 6. IR analysis data of seepage samples

No	Sample Name	The characteristic values (cm-')
1	Adıyaman (Çınarcık)	3398.75 - 2922.54 - 1978.82 - 1109.29 - 871.63 - 601.17 - 668.10 - 712.11 - 797.96 cm^{-1}
2	Adıyaman (Narlık)	1403.57 – 1004,37 – 872,00 – 712,26 – 426,48 – 246,89 – 261,48 – 246,89 cm^{-1}
3	Adıyaman (Alişar)	2168.63 – 2142,23 – 1992,21 – 139,48 – 982,93 – 871,95 – 711,92 – 238,94 – 295,15 cm^{-1}
4	Adıyaman (İçmeler)	2147.71 – 1435.15 – 1034.08 – 879.56 – 728.40 – 273.05 – 298.70 – 219.22 – 282.08 cm^{-1}
5	Adıyaman (Durukaynak)	2925.00 – 2173.95 – 2107.26 – 1795.94 – 1393.49 – 1034.35 – 870.96 – 712.06 - 470.73 – 272.85 cm^{-1}

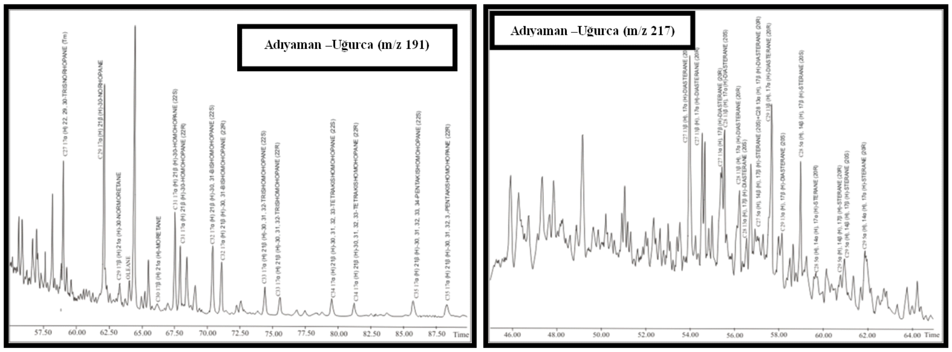

Fig. 3. Adýyaman –Uðurca m/z 191-217 GC-MS chromotogram

The T_{max} values for the hydrocarbon seepage samples of Adýyaman – Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar, Ýçmeler were lower than 435 indicating that the seepage samples were immature (The T_{max} values define the degree of maturation and the temperature of the phasethat the hydrocarbon formation is maximum) (Table 2, Table 5). When GC chromatograms of Adýyaman – Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar, Ýçmeler, Durukaynak samples were investigated; we could get information about the general distribution of hydrocarbon compounds, the type of organic matter and its level of maturation by looking at the peak distribution and height in the chromatograms. While the Pr/Ph ratios were not significant in Adýyaman – Çýnarcýk, Uðurca, Narlýk, Aliþar, Ýzollu, Durukaynak samples, it was lower than 1 in Ýçmeler sample. The n-alkane distribution was between C_{23} and C_{32} in Çýnarcýk, Ýzollu, Aliþar, Durukaynak samples and in all samples light ends were biodegraded except from Ýçmeler. Since the Pr/Ph ratio is lower than 1, Ýçmeler sample was present in a reductive environment. All the samples were immature as single peaks were dominant in all chromatograms (Hunt *et al.*, 1979). GC chromatograms of Adýyaman – Çýnarcýk and Uðurca were given in Fig.1, other chromatograms were shown in the supporting information file. The GC-MS chromatograms of Adýyaman – Çýnarcýk, Uðurca, Narlýk, Ýzollu, Aliþar, Ýçmeler, Durukaynak indicated the character of hydrocarbon distribution, seepage type and level of maturation. C_{30} – C_{35} hopanes were significant and C_{27}-C_{28}-C_{29} steranes were present in all samples (Fig. 2 and Fig. 3 shows the GC-MS chromatograms of Adýyaman – Çýnarcýk and Uðurca samples, respectively. Other chromatograms were given as supporting information). The oleanane peak showed with number 22 was present in all samples except from

Ýçmeler. C_{30} hopane peak was present in all samples (C_{30} hopane indicates high bacterial content). The fact that C_{28} steranes were dominant over C_{27}-C_{29} steranes showed that the source was of lacustrine origin. However, in Narlýk, Ýzollu, Aliþarsamples, C_{29} steranes were dominant over C_{27}-C_{28} steranes and that means the source was of terrestrial origin. Finally, in Ýçmeler ve Durukaynak samples C_{27} steranes were dominant over C_{28}-C_{29} steranes. This dominancy indicates that its source was of marine origin (Seifert *et al.*, 1978; Hunt *et al.*, 1995; Waples *et al.*, 1991; Mackenzie *et al.*, 1980). Infrared spectra that belong to Adýyaman – Çýnarcýk, Narlýk, Ýzollu, Ýçmeler and Durukaynak samples were used to characterize aromatic, diaromatic and poliaromatic hydrocarbons and to determine the effects of sources that constitutes seepage contamination. The IR peak values obtained from these samples were given in Table 6.

The absorption bands identified in the infrared spectrum of Adýyaman – Çýnarcýk sample (Fig.4) were; 601.17, 668.10, 712.11, 797.96, 1109.29, 871.63, 1393.85, 2922.54, 3398.75/cm. As 601.17/cm, 668.10, 712.11 and 797.96/cm bands existed between 558 and 782/cm bands show non-plane C-H bending. Since the bands 1109.29, 871.63/cm observed between 960 and 1170/cm, this indicated the existence of n-alkane ve benzene ring in the structure. Furthermore, the presence of 1393.85/cm band near 1375/cm indicated the methyl groups. Besides, 2922.54/cm (between 2800- 2960/cm) band was assigned to CH_2 - CH_3 stretching mode and 3398.75/cm band was assigned to –OH group. Finally, 1978.82/cm absorption band was assigned to C-H aliphatic groups in the structure (Ganjali *et al.*, 2007; En-Alba-Lurot *et al.*, 1995; Yordanov *et al.*, 2011; Odebunmi *et al.*, 2006; Gruse *et al.*, 1960; Olajire *et al.*, 1998; Olajire, 1998; Kawahara *et al.*, 1969; Kawahara *et al.*, 1970; Kawahara *et al.*, 1972; Lynch *et al.*, 1973; Mattson *et al.*, 1971; Mattson *et al.*, 1970).

From the infrared spectrum of Narlýk sample (Fig.5) following bands were observed; 712,26, 1004,37, 872,00, 1403,57/cm. The 712,26/cm band was assigned to non-plane C-H bending, the absorption bands 1004,37, 872,00/cm were due to the presence of n-alkane and benzene ring. 1403,57/ cm peak was assigned to $–CH_2$ (methylene) groups present in the structure (Ganjali *et al.*, 2007; En-Alba-Lurot *et al.*, 1995; Yordanov *et al.*, 2011; Odebunmi *et al.*, 2006; Gruse *et al.*, 1960; Olajire *et al.*, 1998; Olajire, 1998; Kawahara *et al.*, 1969; Kawahara *et al.*, 1970; Kawahara *et al.*, 1972; Lynch *et al.*, 1973; Mattson *et al.*, 1971; Mattson *et al.*, 1970). The infrared spectra of Adýyaman-Aliþar, Ýçmeler and Durukaynak samples were given as supporting information. Observed bands in the IR spectrum of Aliþar sample were as following; 711.92, 982.93, 871.95,

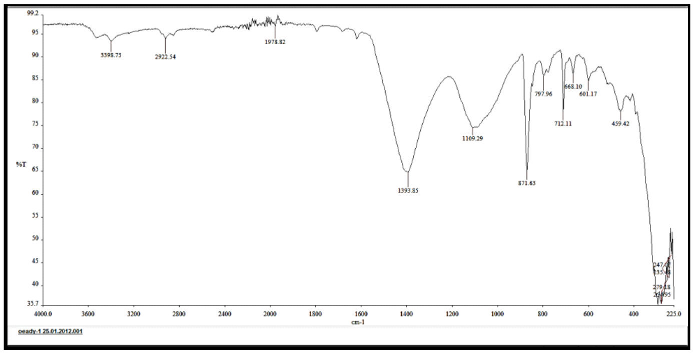

Fig. 4. Infrared Spectrum of Adýyaman – Çýnarcýk

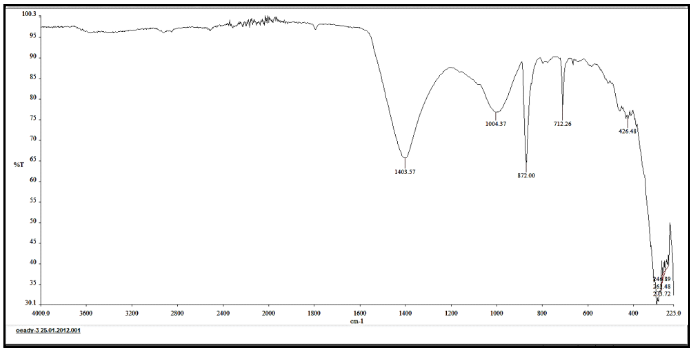

Fig. 5. Infrared Spectrum of Adýyaman – Narlýk

Table7. ICP-OES analysis data of seepage samples (ppm)

No	Sample	Fe	Al	Zn	Mn	B	Ni	Cu
1	Adıyaman (Çınarcık)	5760	11.92	0.216	1.931	1.431	0.507	0.208
2	Adıyaman (Uğurca)	5670	14.34	0.370	0.833	1.243	0.470	0.183
3	Adıyaman (Narlık)	5825	7.218	0.261	1.249	1.275	0.286	0.176
4	Adıyaman (Alişar)	9015	12.85	0.217	2.101	1.337	0.271	0.172
5	Adıyaman (İçmeler)	44380	25.76	0.126	3.231	1.399	0.723	0.180
6	Adıyaman (Durukaynak)	1149	5.251	0.139	0.335	1.367	0.319	0.165

Table 8. Metal concentration values of waterand soil in Turkey and in the world (Swaine *et al.*, 2000)

Metal	Found Value Ranges	Water	Soil	World Coal ppm	Turkey Coal ppm	The amount of metal in the source rock
Cu	0.165-0.302	1.81	0.4	0.0005–0.05	1.5–100	0,057
Zn	0.071-0.618	0.93	0.3	0.005–0.3	5.8–260	0,080
Fe	993-44380	103	23800	-	-	
Mn	0.042-5.013	3.37	0.4	0.005–0.3	-	0,670
Ni	0.286-1.832	-	0.3	0.0005–0.05	3.1–1600	0,095
B	1.100-1.431	-	-	0.005–0.4	22–1200	-
Al	0.275-82.38	54	6.4	-	-	-

1393.48, 2163.68, 2142.23, 1992.21/cm. The observed 711.92 peak was due ton on-plane C-H bending. Moreover, 982.93, 871.95/cm peaks were assigned to n-alkane and benzene ring. The presence of CH_3 (methyl) groups could be seen at 1393.48/cm band. Finally, 2163.68, 2142.23, 1992.21/cm peaks were due to the C-H aliphatic absorption band present in the structure (Ganjali *et al.*, 2007; En-Alba-Lurot *et al.*, 1995; Yordanov *et al.*, 2011; Odebunmi *et al.*, 2006; Gruse *et al.*, 1960; Olajire *et al.*, 1998; Olajire, 1998; Kawahara *et al.*, 1969; Kawahara *et al.*, 1970; Kawahara *et al.*, 1972; Lynch *et al.*, 1973; Mattson *et al.*, 1971; Mattson *et al.*, 1970).

Detected peaks from the infrared spectrum of Ýçmeler sample were 728.40, 1034.08, 879.56, 1435.15 and 2147.71/cm. Same as all samples 728.40/cm peak was assigned to non-plane C-H bending band. Observed bands 1034.08, 879.56/cm showed the presence of n-alkane and benzene ring in the structure. $-CH_2$ (methylene) groups could be seen at 1435.15/cm absorption frequency. In addition, 2147.71/cm peak was assigned to C-H aliphatic absorption bands (Ganjali *et al.*, 2007; En-Alba-Lurot *et al.*, 1995; Yordanov *et al.*, 2011; Odebunmi *et al.*, 2006; Gruse *et al.*, 1960; Olajire *et al.*, 1998; Olajire, 1998; Kawahara *et al.*, 1969; Kawahara *et al.*, 1970; Kawahara *et al.*, 1972; Lynch *et al.*, 1973; Mattson *et al.*, 1971; Mattson *et al.*, 1970). The absorption bands identified in the infrared spectrum of Adýyaman – Durukaynak sample were 712.06, 1034.35, 870.96, 1393.49, 2925.00, 2173.95 and 2107.26/cm. C-H non-plane bending was seen at 712.06/cm. 1034.35 and 870.96/cm peaks were due to the presence of n-alkane and benzene ring in the structure. The presence of CH_3 (methyl) groups could be seen at 1393.49/cm. The observed peak 2925.00/cm was due to the CH_2 - CH_3 stretching band. Furthermore, C-H absorption bands could be seen at 2173.95 and 2107.26/cm (Ganjali *et al.*, 2007; En-Alba-Lurot *et al.*, 1995; Yordanov *et al.*, 2011; Odebunmi *et al.*, 2006; Gruse *et al.*, 1960; Olajire *et al.*, 1998; Olajire, 1998; Kawahara *et al.*, 1969; Kawahara *et al.*, 1970; Kawahara *et al.*, 1972; Lynch *et al.*, 1973; Mattson *et al.*, 1971; Mattson *et al.*, 1970). The presence of Fe, AI, Zn, Mn, B, Ni, Cu metals were detected in the ICP-OES analysis of Adýyaman – Çýnarcýk, Uðurca, Narlýk, Aliþar, Ýçmeler, Durukaynak samples. The related data were shown in Table 7. Ordinary metal concentration values present in water, air and soil were shown in Table 8.

The metal concentrations (Cu, Zn, Fe, Mn, Ni, B, Al) for all samples collected from Adiyaman region

Table 9. The ESR analysis data of the seepage samples

No	Sample	$g=h/B.r/H_r$	G	a
1	Adıyaman (Çınarcık)	714,4842.9,76/3483,1=	2,0020	94,6
2	Adıyaman (Narlık)	714,4842.9,76/3483,1=	2,0020	94,4
3	Adıyaman (Alişar)	714,4842.9,76/(3480,4+2,7)=	2,0020	93,3
4	Adıyaman (Durukaynak	714,4842.9,76/3482,4=	2,0024	93,7

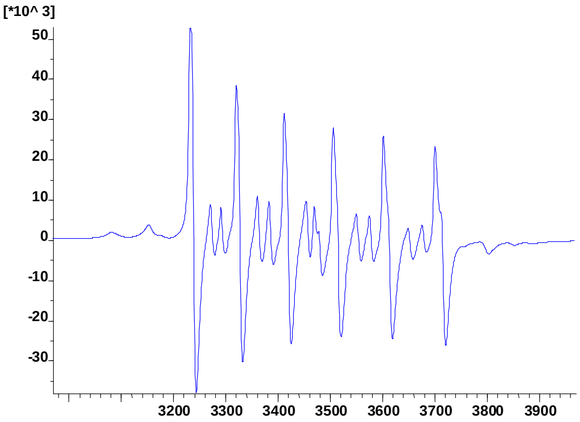

Fig. 6. The ESR spectrum of Çýnarcýk seepage sample

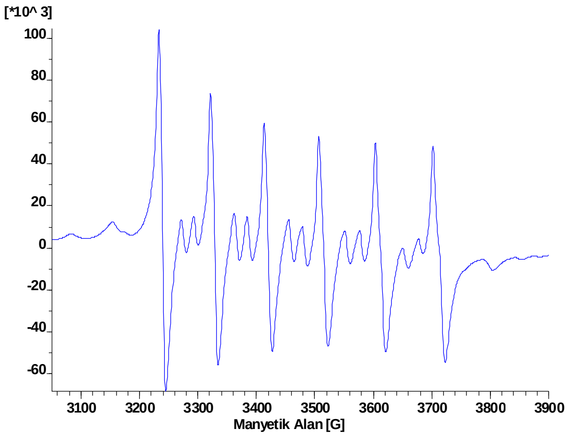

Fig. 7.The ESR spectrum of Narlýk seepage sample

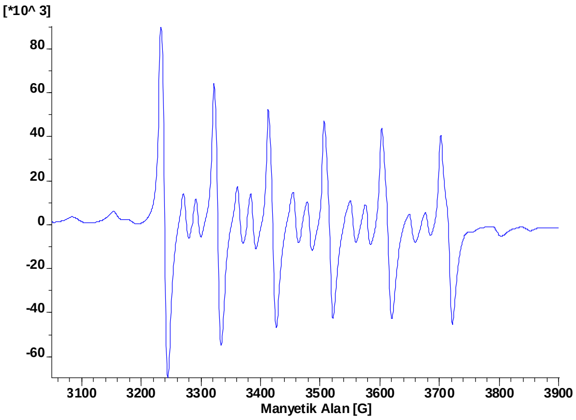

Fig. 8. The ESR spectrum of Alişar seepage sample

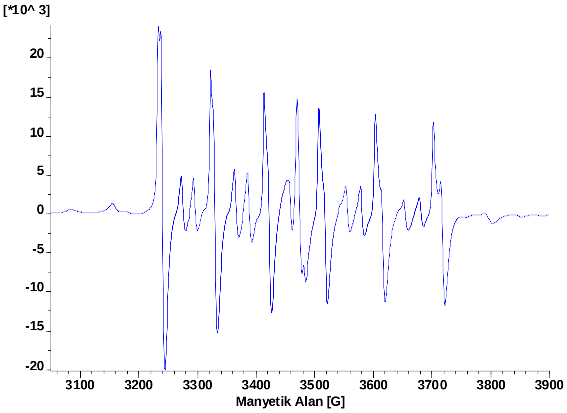

Fig. 9. The ESR spectrum of Durukaynak seepage sample

(Çýnarcýk, Uðurca, Narlýk, Aliþar, Ýçmeler, Durukaynak) were given in Table 7. For natural water to be polluted by seepage its Cu, Zn, Fe, Mn and Al metal concentrations should be over 1.81, 0,93, 103, 3,37, 54 ppm and for soil it should be over 0.4, 0,3, 2380, 0.4, 6.4 ppm respectively. Furthermore, Ni concentration should be over 0,470 ppm for soil to be polluted seepage and Boron (B) does not cause pollution for water or soil (Amorim *et al.*, 2007; Swaine *et al.*, 2000; Duyck *et al.*, 2007; Gülbin *et al.*, 2007). ESR analysis helped us identify Mn^{+2} cation in the collected samples.g value given in Table 9 is a characteristic parameter for different structures and is expressed as spectroscopic splitting factor. g value is very important for structural identification. Free electrons g value is known as 2.0023. For some magnetic ions and free radicals, g value is different from free electron's g value (2.0023). For organic radicals, g value is bigger than 2.0023. However, for paramagnetic ions, g value could be smaller than free electron's value (Polikreti *et al.*, 2004; Engin *et al*., 1999). ESR analysis data (Table 9) and ESR spectra (Fig.6, Fig.7, Fig.8 and Fig.9) for Adýyaman Çýnarcýk, Narlýk, Aliþar, Durukaynak samples were given. According to the ESR analysis results, g value of the Mn^{+2} cation was lower than the free radical's g value in Çýnarcýk, Narlýk and Aliþar samples. Thus, these samples might contain paramagnetic ions. However, since the g value of the Mn^{+2} cation was higher than free radical's g value, Durukaynak sample might contain organic radicals. Besides, the ESR spectrums of the samples recorded in room temperature, gave typical Mn^{+2} ion peak. Namely, ESR spectrums of Mn^{+2} ions display a typical hyperfine sextet and each component of this structure splits into two lines (Polikreti *et al*., 2004; Engin *et al*., 1999; Eichert *et al*., 2000).

CONCLUSIONS

To begin with, TOC and ROCK-EVAL pyrolysis analysis results ensured the detection of organic matter abundance, hydrocarbon generation and source rock formation potential. All of the samples were found to have good hydrocarbon generation potential, to be immature and to be petroleum origin. Additionally, GC analysis led us to see the type of organic matter and level of maturity in the samples by looking at general peak distribution and peak heights of hydrocarbons. All of the samples were found to be immature. GC-MS analysis results were used to detect the level of maturity of oil and organic matter in the samples. These results also provided information about the lithology of the source rock, maturity, oil migration and the type of organic matter. These immature samples have been found to be derived from lacustrine, marine, and terrestrial environments. These three analysis results mentioned above support each other. The infrared anlysis data helped us to identify the structure of the samples. According to the results, the samples have n-alkanes, benzene rings, -OH groups and aliphatic groups. In accordance with the ICP-OES analysis results; the presence of Fe, AI, Zn, Mn, B, Ni, Cu metals were detected. From these metals Fe, AI, Zn, Mn, Ni were found to pollute the environment by hydrocarbon seepage. The ESR data proves Mn values found by ICP-OES. The line thickness used to determine the concentration of Mn+2 in the ESR spectra of the samples is the proof of the Mn content. In the evidence of the results of the analyses mentioned above; it can be said that heavy metals and aromatic compunds having low boiling points inside the hydrocarbon seepages around the province of Adýyaman lead to environmental pollution. Raising awareness and informing the public living in this area should come at the beginning of the measures to be taken for this situation. In addition, since these leaks change the physical structure of the soil, to stop agricultural activities on lands located near and to efficiently convert unproductive lands into fertile lands by cooperating with the institutions such as MTA are some of the measures to be taken. Furthermore, one of the most important measures to be taken is the use of suitable plants to destroy the substances that harm the environment or reduce their negative effects. This method is called as method by treating with plants. Cleaning of the contaminated soil by the technology requiring engineering is very costly process and that leads to visual pollution. Some plant species store the heavy metals coming from the soil inside their bodies, sprouts and leaves in small volumes to re-evaluate later. Thlaspicaerulescens is an example for that.

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