J. Black Sea/Mediterranean Environment
Vol 10: 173- 186

Investigation on the Sediment of Lake Van,Turkey

I - Oil Content

Van Gölü Sedimenti Üzerinde Araştırmalar

I – Petrol İçeriği

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Abstract

In this work hydrocarbon compounds of sediments were investigated in Lake Van. The samples were taken at 7 stations between 10-320 m depths.The highest oil level was found 4.69 µg/g at the station 2. The compounds identified by GC/MS were in aliphatic groups: 17 saturated, 4 cyclic, 5 unsaturated, 5 alcohol, 1 keton, 3 aldehyde and 4 fatty acids and in aromatic groups:1 ring 1, 2 rings 2 and 1 pregnane (5 beta). The compounds identified as: saturated compounds C_5 – C_{43} are homologue series hydrocarbons, whereas alcohol, keton and aldehyde compounds are microbial oxydation products of saturated hydrocarbon compounds. Aromatic groups; phenol, and oxydation products of furane and benzofurane are oil products.
This is the first record for the oil investigation in Lake Van.

Keywords: Lake Van, sediments, hydrocarbons

Introduction

Lake Van is located in the Eastern Anatolia, at 43° E longitude and 38.5° latitude. The lake is 648 m above sea level, with an area of 3524 km^2, a volume of 607 km^3 and a maximum depth of 451 m. It ranks forth among all the closed lakes of the world, following the Caspian and Aral seas and Issykul lake (Degens *et al.*, 1984).

In the north of the lake lies Süphan and western shores Nemrut mountains. The lake has been studied in the four sections as Ercis Gulf, Van Bay, Tatvan Bay and Tatvan Basin.

The investigations made in Lake Van have been in the subjects of Halocen vegetation (Botlema, 1995), microbiolites (Kempe *et al.*, 1991), chemical composition (Jung *et al.*, 1978), diatome as *Navicula gravelli, N. brevis, N. fragilis, Campylosira cymbelli belli* (Öztığ, 1956) and pollen (Zeist and Woldring, 1978), which were characterised prominently as Chenopodiacae Artemisia, Ephedra, Gramineae, Tubuliflorae. Compositae, Umbelliferae and Quercus (Baruch, 1994). The plant in this area was investigated by Nabelek (1923-1929) and Baytop (2001).

Compherensive studies were collected in the book published following the symposium made in Ankara in 1978, organised by M.T.A., the Mineral Research and Exploration Institute of Turkey (Degens and Kurtman, 1978).

The salinity in the lake is 21‰. It is a large soda lake.

Methane was found in Lake Van below 300 m depth (Degens *et al.*, 1978). Various reports on oil reserves in this area were published by MTA as Erzurum – Muş (Şenalp, 1966), Muş – Hınıs (İlker, 1966; Erdoğan, 1967), Hınıs (Tütüncü, 1967), Muş (Dinçer, 1969; Ünal, 1970). There was no information however on the oil content of sea water and sediments of Lake Van. It was suggested that oil and gas seepages occured abundantly in the region but the tectonic setting beneath and around the lake shore was unfavourable for large accumulation of oil deposits (Valeton, 1978; Kurtman, 1978).

A considerable amount (42 700 tons) of fish was estimated to be living in the Lake (Sarı, 2001).

This paper reports the oil content on the sediment of Lake Van.

Material and Methods

Samples from the sediment core were taken at the stations 1-11 situated on the line joining the localities of Adabağ and Reşadiye on 2 Feb. 2002 (Fig. 1). The sampling depths are shown in Table 1.

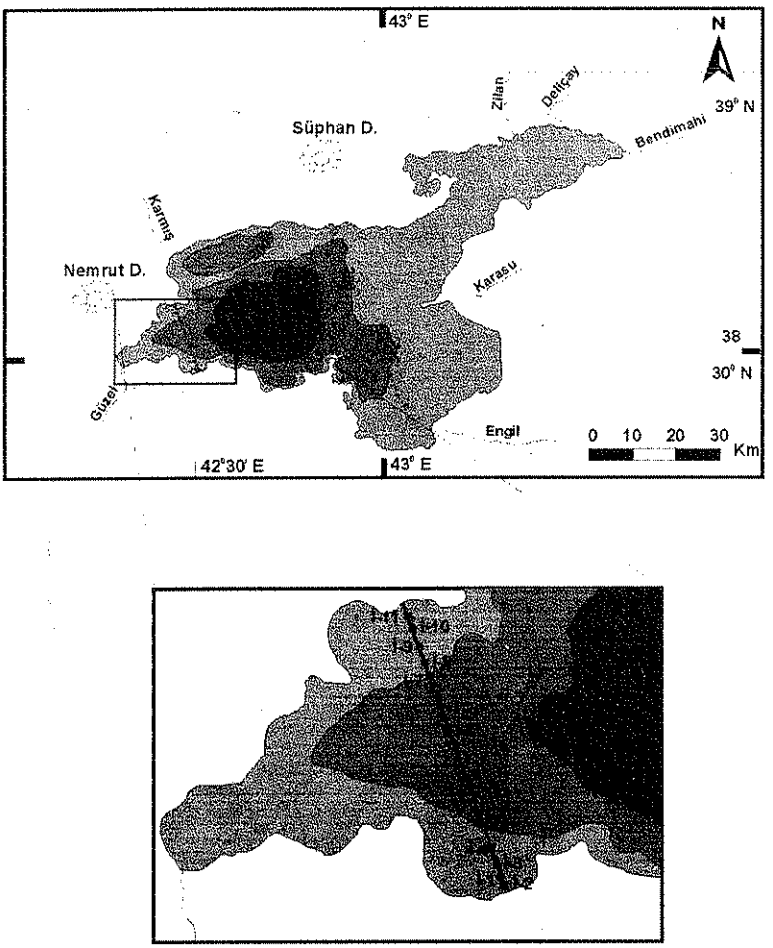

Figure 1. Location of the sampling stations in Lake Van.

Table 1. The sampling depths at the stations in Lake Van

Stations	Depth (m)
1	20
2	10
5	270
6	320
7	200
8	130
9	50
10	20
11	12

1. Extraction

The sample was taken from the top 10 cm of the sediments core. It was mixed with anhydrous sodium sulphate and extracted in Soxhlet apparatus with dichloromethane for 8 h, then filtrated and distilled at 35^0C. The residue was taken with hexane and its intensity measured in UVF spectrophotometer (Shimadzu RF – 1501).

UVF analysis and the standard equations

The reference oil used was Kerkük (Turkey), Iraqi and Iranian in a conc. of 0.6-1.8 µg/ µl in hexane. The standard curve was plotted at 310/360 nm (ex/em) and the equation of the standard curve was taken from the apparatus.

GC/MS analysis

The oil components after quantitation of oil in UVF were determined by GC/MS (HP 6890).

The GC column was an HP 5 MS 30 mx 0.25 mm i.d. (film thickness 0.25 µm) fused–methyl siloxane (Hewlett-Packard). Injections (2 µl) were conducted in the splitless mode with the column held at 50°C for 1 min, from 50-320°C for 10°C/min, 320°C at 5 min; the carrier gas helium (0.8 ml/min). The injector temperature was held at 300° C. Mass spectral data acquired in Selected Ion Monitoring (SIM) mode.

Results

The equation of the standard curves of three different crude oils are given in Table 2.

Table 2.

Reference crude oils	Equations
Iraqi	F_1=488.59 c + 49.758, r^2 = 0.99
Iranian (Heavy)	F1=387.68xÇ+13,181, r^2= 0.99
Kerkük	F1=426.00xC+19.295, r^2= 0.99

Oil contents of Lake Van according to the different equations of reference are shown in Table 3.

Table 3.The oil levels of sediments of Lake Van (µg/g, wet weight) through equivalent reference oil.

Reference Oil / Station	Iraqi	Iranian	Kerkük
1	0.30	0.42	0.37
2	3.26	4.69	4.11
5	0.29	0.40	0.36
6	0.27	0.38	0.34
7	0.49	0.68	0.59
8	0.18	0.25	0.22
9	1.02	1.40	1.23
10	0.36	0.50	0.45
11	0.33	0.47	0.42

The maximum oil level was found at station 2 as 4.69 µg/g trough Iranian oil equivalent. GC/MS chromatograms related to the stations 2,5,7,8 and identified oil compounds are shown in Figures 2-5 and Table 4 respectively.

Table 4. Identified compounds in sediment samples.

Identified Compounds	Sampling stations
1 – Aliphatic Saturated	
C_6 Pentane 2- methyl	2
C_5 Pentane 3 – methyl	2
C_7 Heptane	2
C_8 Octane	2
C_{11} Undecane	7
C_{12} Dodecane	5
C_{22} Docosane	5,8
C_{16} Hexadecane	5
C_{17} Heptadecane	5,8
C_{18} Octadecane	2,5
C_{19} Nonadecane	5,8
C_{20} Eicosane	5
C_{21} Heneicosane 11- (1- etil propyl)	5
C_{27} Heptacosane	2
C_{35} Pentatriacontane	2
C_{43} Tritetracontane	8
Hahnfett	5
Aliphatic cyclic group	
Cyclopentane	2
Cyclohexane	2
Cyclohexadecane	7 ,8
Cycloctane	5
2–Unsaturated	
C_{15} Pentadecene	5
C_{17} Heptadecene	2,8
C_{18} Octadecene	2,5,7,8
C_{20} Nonadecene	2,5
C_{21} Docasene	2

Table 4. Continued

Identified Compounds	Sampling stations
Keton group	
Pentadecanone 6.10.14 tri methyl	7
Alcohol group	
1 – Hexanol 1.2 ethyl	7
Pentadecanol	8
Pentadecanediol	8
Octanethiol	7
Heptadecanol	7,8
Aldehyde group	
Pentadecanal	8
Hexadecanal	8
Octadecanal	8
Acid group	
Hexadecanoic acid (Palmitic acid)	7,8
Octadecanoic acid (Stearic acid)	7
Dodecanoic acid	5
Tetradecanoic acid (Myristic acid)	5,7
2-Aromatic group	
Phenol	5
Isobenzofurandione	2,5,7
Furandione	2
2 (4H) Benzofuranone 5, 6, 7, 7a, tetrahydro – 4,4,7a-trimethyl	7
14-beta- H- Pregnane	2,5,7

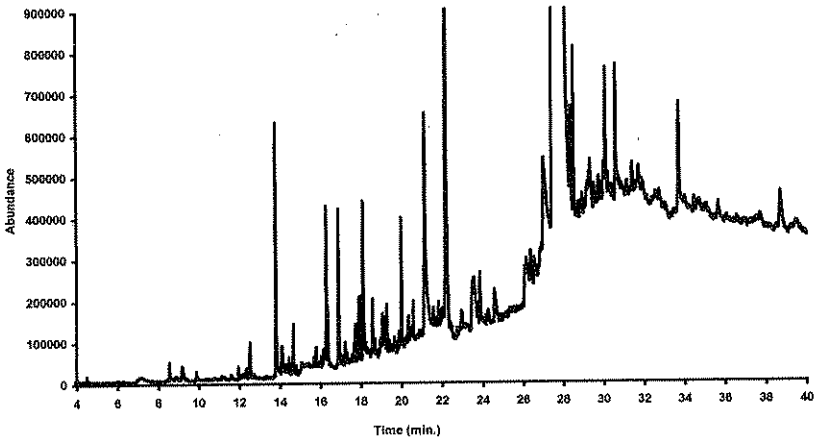

Figure 2. GC/MS chromatogram of the sediment taken from Station 2

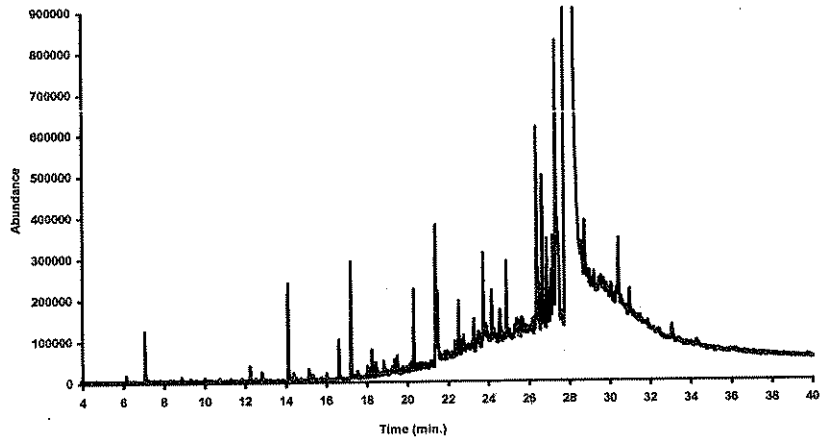

Figure 3. GC/MS chromatogram of the sediment taken from Station 5

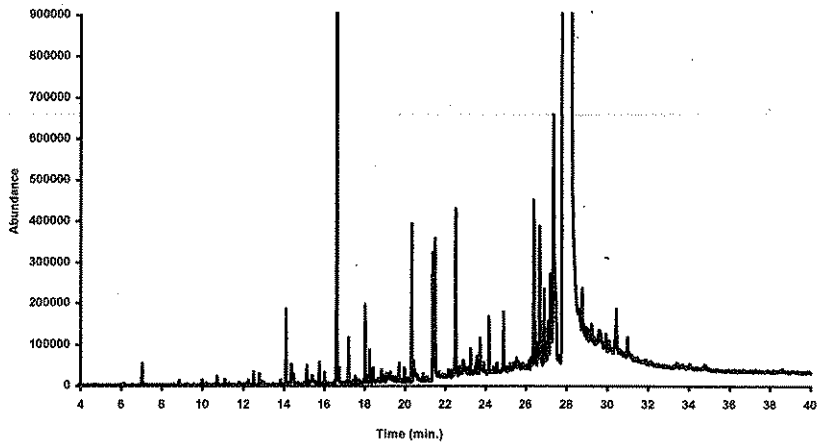

Figure 4. GC/MS chromatogram of the sediment taken from Station 7

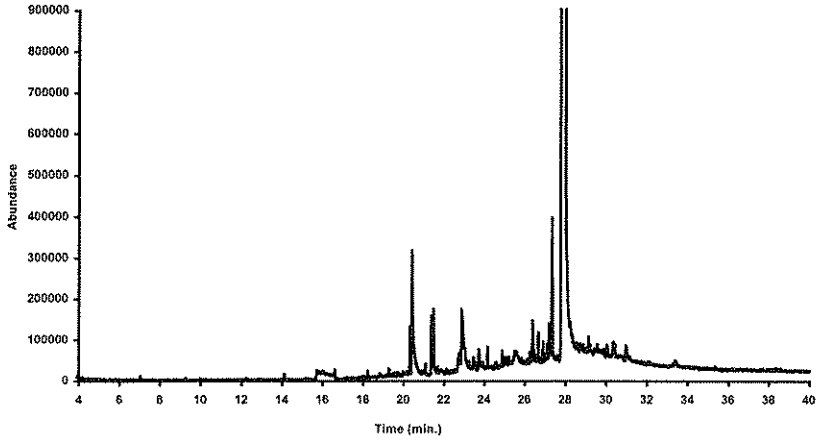

Figure 5. GC/MS chromatogram of the sediment taken from Station 8

The identified compounds are divided into two groups.

1 – Aliphatic compounds

1.1.Saturated C_6 – C_{21} series. These homologue series are found in petroleum and some of them C_{11} – C_{21} also found in marine animals.

1.2.Cyclic groups are petroleum compounds, not found in marine animals.

1.3. Unsaturated hydrocarbons, alcohol, aldehyde and keton groups are microbial oxydation products of saturated group compounds (Gough *et al.*, 1991 a,b).

1.4.Acid groups are oxydation products of aliphatic compounds and also the fatty acids of fish.

2 – Aromatic groups

2.1.Phenol: furandione and benzofurandione derivative which are the oxydation products of furane and benzofurane respectively.

2.2. Pregnane compound is a fish product

Conclusion

The identified compounds in the sediments taken from Lake Van are :

1-homologous series of saturated aliphatic groups belonging to oil and presumably some marine animals;
2-branched aliphatic hydrocarbons of oil components;
3-oxydation products of hydrocarbons such as alcohols, aldehydes and ketons;
4-fatty acids belonging to plankton and marine animals as well as presumably oxydation products of aliphatic compounds of oil;
5-Cyclic aliphatic and three aromatic compounds as sign of oil compounds;
6- pregnane compound of fish.

The rare ship traffic on the lake can be considered as a negligeable source of oil pollution. Therefore the origins of the hydrocarbon compounds in sediments must be sought by future investigations.

This work is the first record on oil in sediment of Lake Van.

Acknowledgmet

The authors thank TUDAV (Turkish Marine Research Foundation) for the supply of sediment samples for this study.

Özet

Bu çalışmada Van Gölü sedimentinde hidrokarbon bileşenleri araştırılmıştır. Denenen 11 istasyondan en yüksek petrol kirliliği 2 numaralı istasyonda 4.69 µg/g bulunmuştur. GC/MS analizi sonucunda bu istasyonda 17 doymuş zincirde alifatik, 4 alifatik siklik grup, doymamış 5 alkol, 3 aldehit, 1 keton, 4 asit ve aromatik gruptan 3 ve pregnan gruptan 1 madde saptanmıştır. Tespit edilen bu maddelerden alifatik gruba ait C_6 ve C_{21} arası bileşenlerin yanında bunlara ait oksidasyon ürünlerinden alkol, aldehit, keton ve asit grubu maddeler tespit edilmiştir. Diğer oksidasyon ürünleri arasında asit grubundan yağ asitlerinin mevcudiyeti bu gölde bulunan deniz canlılarına ait olabildiği gibi alifatik petrol komponentlerinin oksidasyon ürünü de olabilir. Sediment örneklerinde tespit edilen alifatik homolog dizideki maddelerin ve aromatik grup bileşiklerinin bulguları bu hidrokarbon bileşiklerinin petrole ait olduğuna işarettir. Yukarıda belirtilen bulgular Van Gölü sedimentinde petrol hidrokarbonlarına ait bulgular daha başka çalışmalar yapılmasını gerektirmektedir.
Bu çalışma Van Gölü sedimentinde yapılan ilk petrol çalışmasıdır.

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Received: 08.12. 2003
Accepted:05.01.2004