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The Volatile Petroleum Hydrocarbons in Marine Algae Around Turkish Coasts

Türkiye Sahilleri Deniz Alglerinde Uçucu Petrol Hidrokarbonları

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Abstract

Volatile hydrocarbons were investigated in 14 marine algae collected in the Black Sea, Dardanelles and Aegean Sea. The algae were extracted with dichloromethan in Soxhlet for 8 h. The extracts were distilled and the volatile compounds of the residue were separated by steam distillation. The distillates were extracted for ether and distilled. The residue analyzed by Gas chromatography/Mass Spectrophotometry (GC/MS).

The identified substances are: in aliphatic group: 19 linear, 20 branched, 19 cyclic alkenes, 18 alkenes, 2 alcohols, 12 aliphatic aldehydes, 2 ketones, on aromatic group: 31 mono ring, 16 naphthalene derivatives, 4 indan derivatives, 2 three rings and three sulfur containing aromatic compounds. Additionally 1 aromatic aldehyde, phenyl alkene derivative were identified.

The Pristane/Phytane (Pr/Ph) ratio and the compounds mentioned above inadequate the oil contamination of algae.

Comparison of the data published since 1960 with our results shows that the numbers of detected oil compounds are increasing. The anomalous on the hydrocarbons detected in algae can be attributed to oil contamination.

Besides these oil compounds (Exogenic), some toxic compounds as phthalates and nonyl phenol were detected in algae sample. The latter compound is originated from degradation of non ionic surfactant. The all oil compound identified in algae were originated from the oil pollution. The origin of some alkenes, aldehydes, alcohols are suspect. These findings show that the algae can be used as indicator in sea water pollution.

Keywords: Marine algae, volatile hydrocarbons, GC/MS.

Introduction

Hydrocarbons originating from sea environment can be grouped in two classes. Firstly biogenic hydrocarbons (biogeneous, autochthonous) synthesized by marine organisms as various fish, planktons, algae but these biogenic compounds are not particularly abundant. Secondly exogenic (anthropogenic, allochthonous) compounds enter to the sea as the results of from

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atmosphere, marine traffic, tanker accident, refinery, industrial and city sewage. Aromatic compounds especially PAHs are characteristic for petroleum. Marine organism do not synthesized these compounds. Anthropogenic hydrocarbons may cause changes in marine flora and fauna. Marine organisms are capable of accumulation oil hydrocarbons in their body (Miranov et al. 1981).

Hydrocarbon contents of marine algae were investigated by numerous authors (George1961; Clark and Blumer 1967, 1973, Youngblood 1971, Di Salvo 1976, Clark and Finley 1974, 1979, Goldberg 1976, Gearing et al. 1976, Rossi et al. 1978, Thomas 1978, Miranof et al. 1981, Jackson 1989, Peckol et al. 1990, Talvari 1992, Güven et al. 1998, Binark et al. 2000, Kamenarska et al. 2002, Broadgate et al. 2004, Crespo and Yusty 2004). These authors discussed the contents and dominant hydrocarbon in algae. The differentiation of the origin autochthonous pollutant made on the content particularly normal paraffin or cyclic hydrocarbons (Clark and Finley 1974).

Biogeneous hydrocarbons of the marine system, alkenes (mono, di and cyclic) were originated from algae (Blumer et al. 1971). One characteristic of crude oils that distinguishes them from biogeneous hydrocarbons is their content in cyclo alkenes and aromatic compounds (Goldberg 1976).

Clark and Blumer (1967) reported that red algae contained large concentration of n-C_{15} and n-C_{17}, and minimum n-C_{21} concentration and then increases to a secondary maximum in the n-C_{27} region (Youngblood 1971). Gearing et al. 1976 found similarly to Clark and Blumer (1976) C_{17} alkane is high in *Sargassum sp.* and C_{15} in brown algae.

In algae, phytane amount is less than pristane Clark and Finley (1973), Di Salvo et al. 1976 were obtained the same results.

n-C_{17} / Pristane and n-C_{18}/ Phytane ratio were low in algae. The dominant hydrocarbon is C_{15} in brown and C_{16} in red and C_{17} in green algae (Youngblood 1971). They found polyolefinic hydrocarbon levels are high in red, C_{19} and C_{21} in brown algae.

Youngblood and Blumer (1973) suggested that hydrocarbon composition of the algae differ greatly from that of fossil fuels in it simplicity and predominately unsaturated nature. The high amount of olefinic heneicosohexane (HEH) in *Fuccus sp.*, heneicosopentane (HEP) in *Ascophyllum sp.* (Youngblood 1971).

Oil pollution in algae was investigated after tanker accident as Nassia occurred in March 1994 at Istanbul. Güven et al. 1998 and after prodigy in June 1989 (Peckol et al. 1990).

Di Salvo et al. (1976) found aromatic hydrocarbon in algae polluted. Miranow et al. 1981 are reported that the algae collected the clean and polluted area; the range of n-C_{17} is high from polluted area.

Biogeneous hydrocarbons found in the algae examined earlier in this paper were hordenine from *Phyllophora nervosa (P.crispa)* (Güven et al. 1970; Percot et al. 2007), from *Gelidium crinale* (Yalçın et al. 2007), β–phenylethylamine from, *Gelidium crinale*, *Polysiphonia morrowii*, *Polysiphonia tripinnata*, *Gracilaria bursa-pastoris*, *Halymenia floresii*, *Phyllophora crispa (Percot et al. 2009),* Loliolide from *Phyllophora crispa, Boergeseniella fruticulosa, Polysiphonia morrowii, Gelidium crinale, Hypnea musciformis, Corallina granifera, Halymenia floresii, Cutleria multifida, Dictyota dichotoma, Taonia atomaria, Cystoseira mediterranea, Sporochnus pedunculatus, Enteromorpha compressa* (Percot et al. 2009), fatty acids (Yazıcı et al. 2007) and new sterol glucoside from *Gracilaria verrucosa* (Hudson) Papenfuss (Aydoğmuş 2008).

Marine algae can be used as indicators of petroleum pollution as it is possible to separate the biogenic paraffin hydrocarbons from pollution hydrocarbons (Clark and Finley 1979).

In this paper is reported the volatile hydrocarbon compounds in marine algae.

Materials and Methods

Algal Material

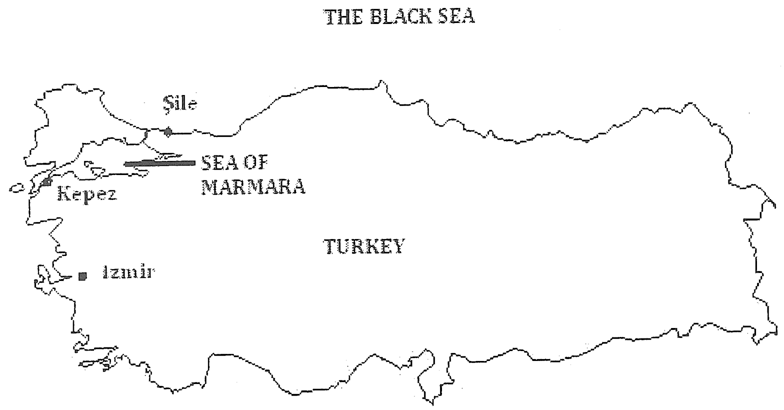
The algae samples were collected in Jan. 2005 except *Gracilaria verucosa* in 2002.

The stations of algae are listed in Table 1 and location in Fig 1.

Table 1. The stations of algae collected in 2005.

<table>
<tr><th>Station</th><th>Division</th><th>Algae</th></tr>
<tr><td rowspan="7">Şile
(The Black Sea)</td><td rowspan="3">Chlorophyta</td><td>Ulva rigida C. Agardh</td></tr>
<tr><td>Enteromorpha muscoides (Clemente) Cremades</td></tr>
<tr><td>Enteromorpha linza (Linnaeus) J.Agardh</td></tr>
<tr><td rowspan="3">Rhodophyta</td><td>Gelidium pulchellum var claviferm (Turner) Kützing</td></tr>
<tr><td>Polysiphonia elongata (Hudson) Sprengel</td></tr>
<tr><td>Corallina mediterranea Ellis& Solander</td></tr>
<tr><td>Phaeophyta</td><td>Cystoseira barbata (Stackhouse) C.Agardh</td></tr>
<tr><td rowspan="7">Kepez
(Dardanalles)</td><td>Chlorophyta</td><td>Codium fragile (Suringar) Hariot</td></tr>
<tr><td rowspan="3">Rhodophyta</td><td>Peyssonnelia squamaria (S.S.Gemelin) Decaisne</td></tr>
<tr><td>Rhododymenia corallina var. spathulata (Zanardini) Ardissone</td></tr>
<tr><td>Phyllophora nervosa (A.P. de Candolle) Greville</td></tr>
<tr><td rowspan="3">Phaeophyta</td><td>Cystoseria barbata (Stackhouse) C. Agardh</td></tr>
<tr><td>Colpomenia peregrina Sauvageau</td></tr>
<tr><td>Zanardinia prototypus (Nardo) Nardo</td></tr>
<tr><td>İzmir
(Aegean Sea)</td><td>Rhodophyta</td><td>Gracilaria verrucosa (Hudson) Papenfuss</td></tr>
</table>

Fig. 1. Sampling station



Extraction

60 g powdered algae sample were mixed with 20 g anhydrous sodium sulfate and extracted with dichloromethane in Soxhlet apparatus for 8 h. The extract was distilled at 40 °C. The volatile compounds of the residue were separated by steam distillation. The distillate was extracted with diethyl ether. The ether extract was distilled at 40 °C and the residue was taken with 1ml hexane and applied to GC/MS.

Materials

All solvents used were at Merck products (Darmstadt, Germany), sodium sulfate was supplied by BASF (Baden, Germany)

Gas chromatography/Mas spectrometry (GC/MS)

The gas chromatography mass spectrometer (HP 6890 Series GC System; Hewlett Packard, Willmington, DE, (USA) was fitted with sn electronic pressure control a mass selective detector (HP 5972 A; ionization energy: 70 eV; HP-PONA capillary column (50m 0.25 μm film thickness). The chromatographic conditions were: sample size 2 μl, injection port temperature 280 °C, configured for split injection; initial oven temperature 40 °C rising to 280 °C at 8°C / min, final hold of 20 min. Helium was used as carrier gas (1 ml/min).

The volatile compounds in algal extract were identified by comparing the retention time and its spectrum with HP memory.

Results and Discussion

The identified volatile compounds by GC/MS in algae extracts are shown in Table 1-11.

Table 1.Linear alkyl
Table 2.Branched alkyl
Table 3.Cyclic aliphatic
Table 4.Alkenes
Table 5.Aliphatic aldehydes
Table 6.Aliphatic ketones
Table 7.Aromatic hydrocarbon
Table 8.Naphthalenes derivatives
Table 9.Anthracene/ phenanthrene
Table 10.Sulfur containing compounds
Table 11.Phenols and nonyl phenol and Phthalates

Number of algae cited in the tables are:
1.*Ulva rigida,* 2.*Enteromorpha muscoides,* 3.*Enteromorpha linza,* 4.*Gelidium pulchellum var.claviferum,* 5.*Polysiphonia elongata,* 6.*Corallina elongata,* 7.*Cystosira barbata,* 8.*Codium fragile,* 9.*Peyssonnelia squamaria,* 10.*Rhodymenia corallina var.spathulata,* 11.*Phyllophora nervosa,* 12.*Colpomenia peregrina,* 13.*Cystoseira barbata,* 14.*Zanardinia prototypus,* 15.*Gracilaria verrucosa*
G: Green, R: Red, B: Brown

Table 1. Linear alkyl compounds in algae

	Şile							Dardanelles							İzmir
	G		R				B	G	R		B				R
Aliphatic Hydrocarbons \ Algae Species	*Ulva rigida*	*Enteromorpha muscoides*	*Enteromorpha linza*	*Gelidium pulchellum var. claviferum*	*Polysiphonia elongata*	*Corallina mediterranea*	*Cystoseira barbata*	*Codium fragile*	*Peyssonnella squamaria*	*Rhodymenia corallicola var. spathula*	*Phyllophora nervosa*	*Colpomenia peregrina*	*Cystoseira barbata*	*Zanardinia prototypus*	*Gracilaria verrucosa*
Algae number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Nonane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Decane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Undecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Dodecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Tridecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Tetradecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Pentadecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hexadecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Heptadecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Octadecane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Nonadecane		+	+	+	+	+	+	+		+	+	+	+		+
Eicosane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Heneicosane	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Docasone		+	+	+	+	+	+	+	+	+	+	+	+	+	+
Tricosane		+	+	+	+	+	+	+	+	+		+			
Tetracosane	+	+	+	+	+	+	+	+							
Pentacosane	+	+	+	+	+	+	+								
Hexacosane	+														
Heptacosane	+	+													

Table 2. Branched alkanes in algae.

	Şile							Dardanelles							İzmir
	G		R				B	G	R		B				R
Algae number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
4 Methyl nonane														+	+
2 Methyl decane								+			+		+	+	+
4 Methyl decane				+									+	+	+
2 Ethyl decane							+								
2 Methyl tridecane											+				
2 Methyl tetradecane															+
2 Methyl hexadecane				+											
3 Methyl heptadecane					+										
7 Methyl heptadecane								+			+				
8 Methyl heptadecane															+
3 Methyl eicosane							+								
2,4 Dimethyl heptane										+					+
2,6 Dimethyl octane														+	+
2,6 Dimethyl undecane								+			+				
2,6,7 Trimethyl decane							+								
2,7,10 Trimethyl dodecane														+	
2,6,10 Trimethyl pentadecane (Nor-pristane			+				+								
2,6,10,14 Tetramethyl pentadecane(Pristane)	+	+	+	+	+		+	+	+	+	+	+	+	+	
2,6,10,14 Tetramethyl hexane (Phytane)	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2,6,10,15,19,23 Hexamethyl tetracosane(Squalen)									+	+			+		

Table 3. Cyclic aliphatic compounds in algae.

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Cyclo dodecane		+						+		+				+	
Cyclo tetradecane								+			+	+			
Cyclo pentadecane							+				+				
Cyclo hexadecane							+				+		+		+
Cyclo eicosane							+								
Cyclo tetracosane	+	+													
Ethyl cyclo decane					+										
Ethyl cyclo dodecane								+							
Buthyl cyclo pentane								+							
Buthyl cyclo hexane														+	+
Pentyl cyclo hexane								+			+				
1 Ethyl 2 methly cyclodecane				+											
1,1 Dimethyl 2 prpyl cyclohexane															+
1(Oetyl nonyl) cyclohexane					+										
Isopently cyclopentane								+							+
1, 3 Cyclooctadien														+	
1, 3, 5, 7 Cyclooctatetraene		+	+	+		+	+		+		+				+
Decahydronaphthalene			+				+			+			+		+
Cis_decahydronaphthalene				+							+				

Table 4. Alkenes in algae

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1 Tetradecene								+							
1 Pentadecene				+		+	+	+							
1 Hexadecene							+					+			
3 Hexadecene	+													+	
7 Hexadecene				+				+							
1 Heptadecene	+					+		+	+		+		+	+	
1 Heptadecene	+	+	+	+	+	+	+			+	+	+	+	+	+
1 Octadecene	+			+	+	+	+	+		+	+			+	
3 Octadecene									+		+				
5 Octadecene									+						
1 Nonadecene					+	+	+	+			+				
Cis 2 Nonadecene		+													
(Z) 2 Dodecene											+				
3 Eicocene					+										
9 Tricocene							+								
2,4 Dimethyl 1 heptene										+					
1,3 Tetradecadine							+								
1, 4, 8 Dodecatriene														+	

Table 5. Aliphatic aldehydes in algae

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Hexanal								+		+			+	+	
Heptanal								+		+				+	
Decanal								+							
Dodecanal								+	+			+		+	
Tridecanal					+				+		+	+		+	
Tetradecanal					+	+		+	+	+	+	+		+	
Pentadecanal													+	+	
Hexadecanal							+				+	+	+		
Octadecanal								+			+			+	
2 Hexanal												+		+	
Trans 2 hexanal					+	+	+	+							
9 Octadeanal									+		+			+	

Table 6. Aliphatic ketones in algae

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2Hexanon				+		+	+	+	+	+	+	+		+	+
3Hexanon		+		+		+	+	+		+		+	+	+	+

Table 7. Aromatic hydrocarbon in algae

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae species / Aromatic hydrocarbons	*Ulva rigida*	*Enteromorpha muscoides*	*Enteromorpha linza*	*Gelidium pulchellum var. clasiferum*	*Polysiphonia elongata*	*Corallina mediterranea*	*Cystoseira barbata*	*Codium fragile*	*Peyssonnella squamaria*	*Rhodymenia corallicola var. spathulata*	*Phyllophora nervosa*	*Colpomenia peregrina*	*Cystoseira barbata*	*Zanardinia prototypus*	*Gracilaria verrucosa*
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Methyl benzene (Toluene)	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1 Methyl 2 propyl benzene (o propyl toluene)				+				+		+		+	+	+	+
1 Methyl 3 propyl benzene (m propyl toluene)	+		+	+					+	+	+		+	+	+
1 Methyl dodecyl benzene (2 phenyl tridecane)				+		+									
2 Methyl 1 ethyl benzene (o ethy tolaene)				+	+	+	+		+	+		+	+		+
3 Methyl 1 ethyl benzene (m ethyl touene)														+	
1.2 Dimethyl benzene (o-xylene)					+		+				+				
1,3 Dimethyl benzene (m- xylene)	+	+	+		+		+	+	+	+					
1,4 Dimethyl benzene(p-xylene)	+	+	+	+		+		+		+	+	+	+	+	+
1,3 Dimethyl 2 ethyl benzene (2 ethyl-m-xylene)				+				+					+		+
1,4Dimethyl 2 ethyl benzene (2 ethyl-p-xylene)			+	+					+	+	+		+	+	
2,3Dimethyl 1 ethyl benzene (3 ethyl-0-xylene)		+	+		+	+	+	+	+	+		+		+	+
3,5Dimethyl 1 ethyl benzene (5 ethyl-m-xylene)				+			+	+			+		+		
1,2,3 Trimethyl benzene (Hemellitol)			+		+			+			+			+	+
1,2,4 Trimethyl benzene (Pseudocumen))		+		+	+	+	+	+	+	+	+	+	+		+
1,3,5 Trimethyl benzene	+				+	+		+		+				+	
1,2,3,4 Tetramethyl benzene (Prehnitol))	+		+	+	+					+		+			+
1,2,4,5Tetramethyl benzene (Duren)						+	+	+	+		+	+	+	+	+
Ethyl benzene	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1,2 Diethyl benzene			+					+			+		+		+
1,3 Diethyl benzene	+			+		+	+			+		+		+	
1,4 Diethyl benzene		+													
Propyl benzene	+	+	+	+		+	+	+		+	+	+	+	+	+
Isopropyl benzene (Cumene)		+	+	+	+			+			+		+	+	+
1 Propyl decyl benzene (4 phenyl tridecane)				+											
Butyl benzene								+		+					
1 Butyl octyl benzene (5 phenyl dodecane)						+									
1Butyl nonyl benzene (5 phenyl tridecane)			+	+											
1 Hexyl heptyl benzene (7phenyl tridecane)						+									
1 Methyl 2 phenyl cyclopropan											+	+		+	+
C3-benzene	+	+	+	+			+	+		+	+	+	+	+	+

Table 8. Naphthalenes derivatives in algae.

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Naphtalene	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1 Methyl naphtalene					+								+	+	+
2 Methyl naphtalene	+	+	+	+			+	+	+		+				+
1,2 Dimethyl naphtalene												+			
1,3 Dimethyl naphtalene	+			+			+								
1,5 Dimethyl naphtalene		+		+							+				+
1,6 Dimethyl naphtalene										+		+			+
1,7 Dimethyl naphtalene										+		+		+	
1,8 Dimethyl naphtalene	+			+									+		
2,3 Dimethyl naphtalene						+		+	+		+			+	
2,6 Dimethyl naphtalene		+			+	+	+	+			+		+		
2,7 Dimethyl naphtalene			+				+								+
1,4,6 Trimethyl naphtalene							+								
2,3,5 Trimethyl naphtalene											+				
2,3,6 Trimethyl naphtalene .				+				+							
1 Ethyl naphtalene				+							+				

Table 9. Anthracene/ phenanthrene in algae

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2Hexanon				+		+	+	+	+	+	+	+		+	+
3 Hexanon		+		+		+	+	+		+		+	+	+	+

Table 10. Sulfur containing compounds in algae

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
3 Methyl dibenzothiophene		+				+		+	+	+		+	+	+	+
Benzothiazole	+	+	+	+	+			+	+		+			+	
Benzothiozolon	+	+				+			+	+	+	+	+	+	+

Table 11. Phenols and nonyl phenol and Phthalates

	Şile							Dardanelles							İzmir
	G			R			B	G	R			B			R
Algae number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Hydroxy benzene (Phenol)	+			+	+	+	+	+		+	+	+	+	+	+
1 Hydroxy 2 methyl benzene (o-Cresol)					+										
1 Hydroxy 3 methyl benzene (m-Cresol)									+		+			+	+
1 Hydroxy 4 methyl benzene (p-Cresol)								+							
Nonyl phenol	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Di ethyl phthalate					+										
Di butyl phthalate		+					+				+		+	+	+
Iso butyl phthalate	+		+	+			+		+		+	+	+	+	
N butyl iso butyl phthalate	+		+		+					+		+			

Table 12 show Pristane and Phytane(Pr/Ph)ratio in algae experimented.

Table 12 show Pristane and Phytane(Pr/Ph)ratio

			Pr / Ph	C_{18} / Ph
1	Şile	*Ulva rigida*	9,7	2,12
2		*Enteromorpha muscoides*	7,64	2,04
3		*Enteromorpha linza*	0,99	1,36
4		*Gelidium pulchellum var. claviferum*	0,34	1,43
5		*Polysiphonia elongata*	0,94	1,48
6		*Corallina elongata*	-	1,44
7		*Cystoseira barbata*	1,09	1,4
8	Çanakkale	*Codium fragile*	6,13	1,79
9		*Peyssonnelia squamaria*	1,26	1,21
10		*Rhodymenia corallicola var. spathulata*	0,81	1,47
11		*Phyllophora nervosa*	0,83	1,57
12		*Colpomenia peregrina*	1,01	1,11
13		*Cystoseira barbata*	1,1	1,8
14		*Zanardinia prototypus*	1,307	0.292
15	İzmir	*Gracilaria verrucosa*	-	0.9

Figures 2-16 show the series of aliphatic hydrocarbons on the GC/MS chromotogram of algae.

Figure 2.GC/MS chromatogram of *Ulva rigida.*

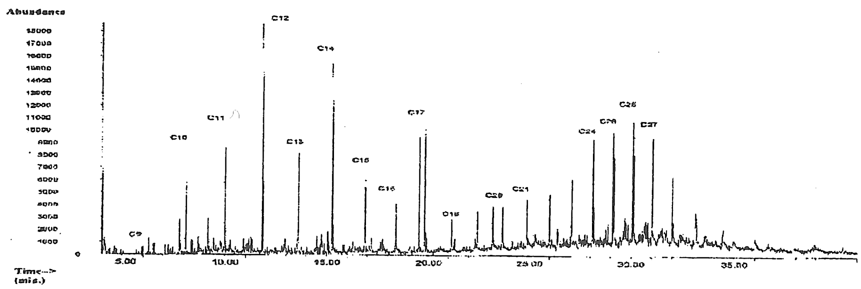


Figure 3. GC/MS chromatogram of *Enteromorpha muscoides.*

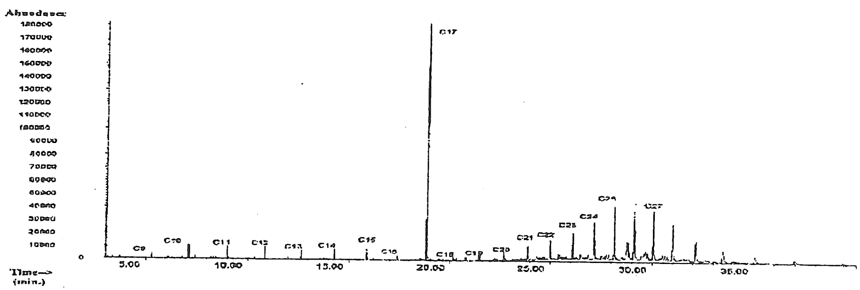


Figure 4. GC/MS chromatogram of *Enteromorpha linza.*

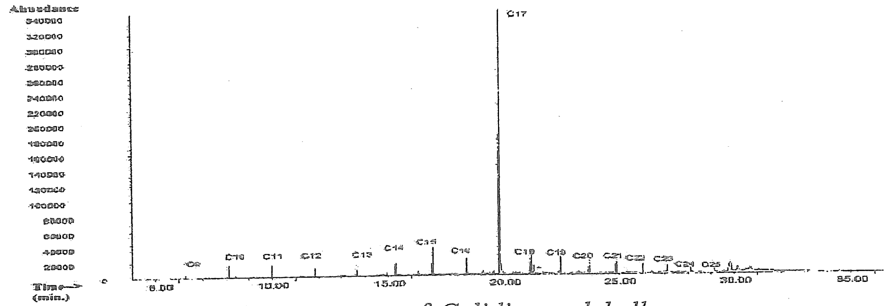


Figure 5. GC/MS chromatogram of *Gelidium pulchellum var.*

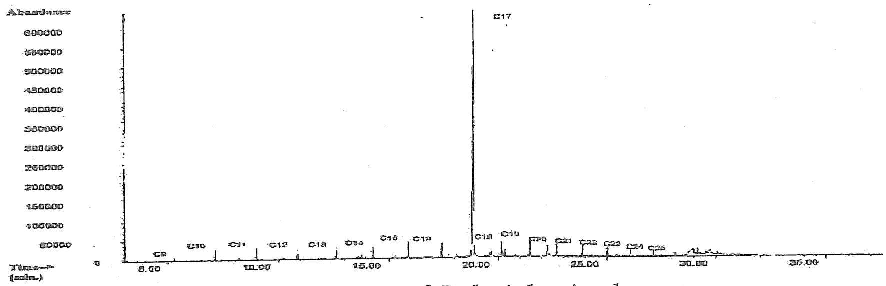


Figure 6. GC/MS chromatogram of *Polysiphonia elongata.*

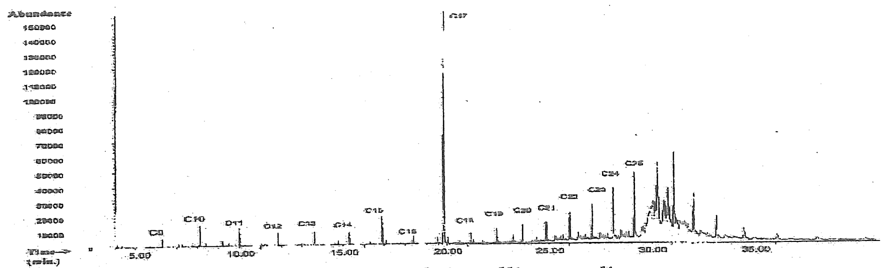


Figure 7. GC/MS chromatogram of *Corallina mediterranea.*

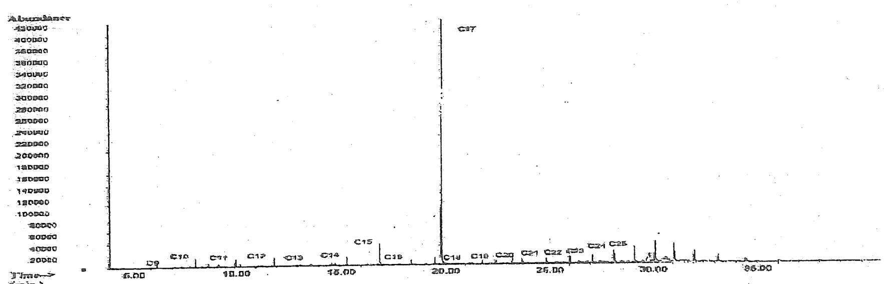


Figure 8. GC/MS chromatogram of *Cystoseria barbata.*

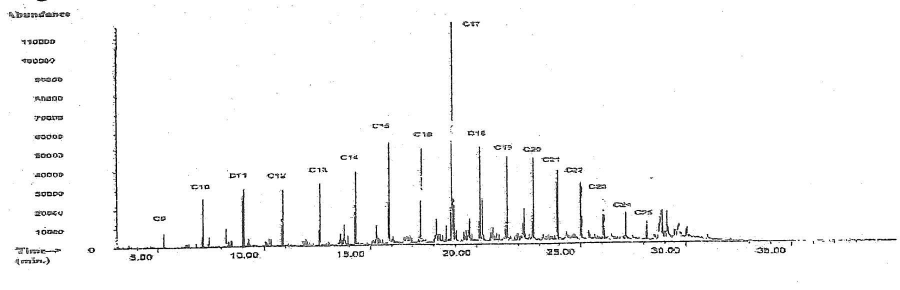


Figure 9. GC/MS chromatogram of *Codium fragile*.

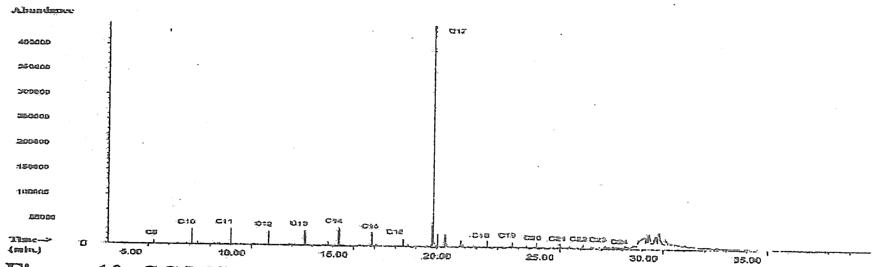


Figure 10. GC/MS chromatogram of *Peyssonnelia squamaira.*

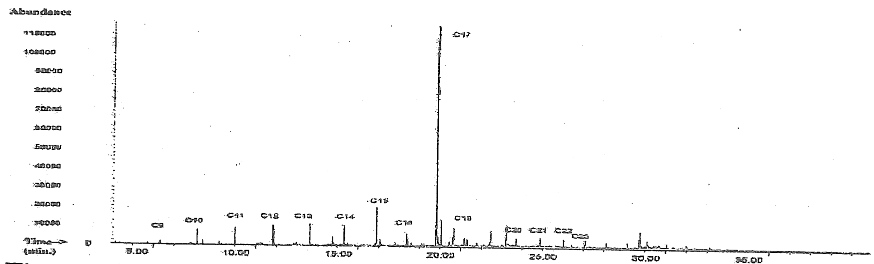


Figure 11. GC/MS chromatogram of *Rodymenia corallicola var.*

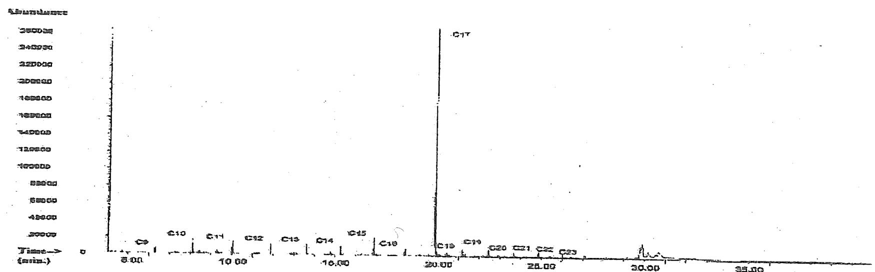


Figure 12. GC/MS chromatogram of *Phyllophora nervosa.*

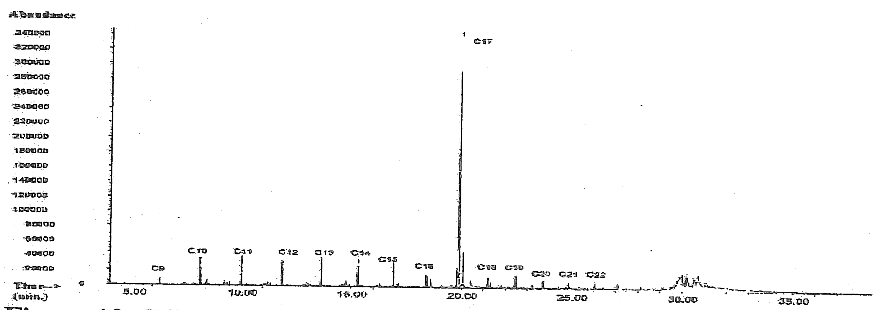


Figure 13. GC/MS chromatogram of *Colpomenia peregrina.*

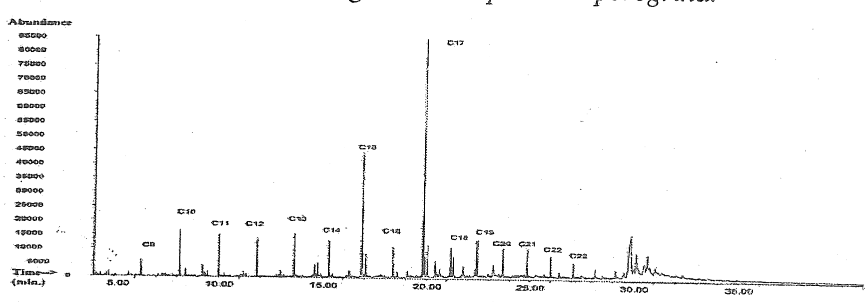


Figure 14. GC/MS chromatogram of *Cystoseria barbata.*

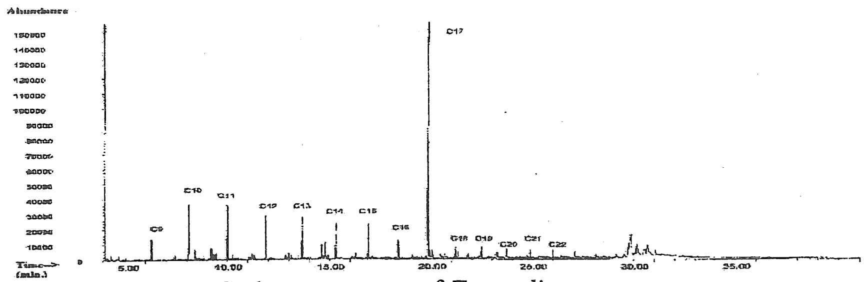


Figure 15. GC/MS chromatogram of *Zanardina protypus.*

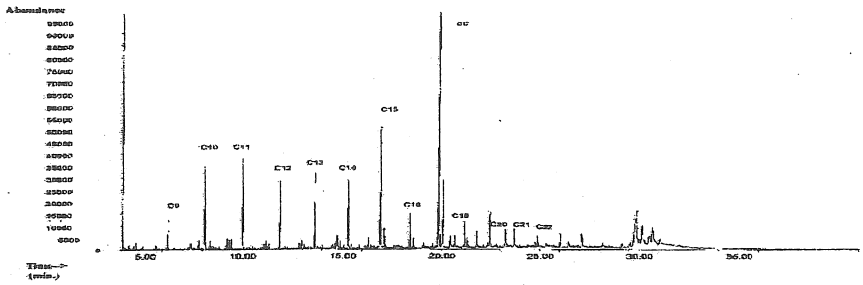
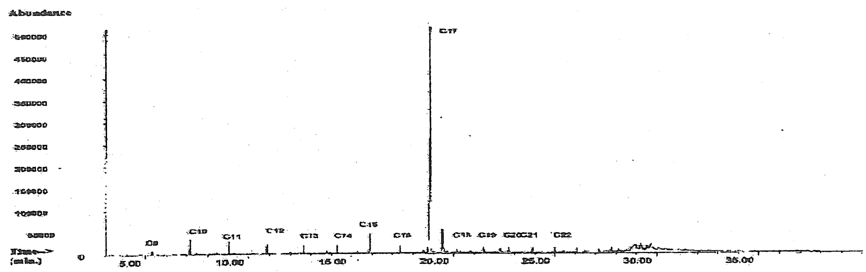


Figure 16. GC/MS chromatogram of *Gracilaria verrucosa.*



Linear n-alkenes C_9-C_{25} compounds were detected in the algae tested (Fig 2-16). Regular series of n- alkanes were found in all algae.

Predominant alkanes in aliphatic groups detected are:
C_{12}: *U. rigida*
C_{17}: *E.muscoides, E. linza, G. pulcellum, P. ellongata, C. mediterranea, C. barbata, C. fragile, P. squamaria, R. corallicola, P. nervosa, C. peregrina, Z. prototypus, G. verucosa.*

We found that n- C_{17} hydrocarbon is predominant in algae tested as findings of Claring et al. (1976). GC/MS chromatograms of algae show the major peaks of C_{17} in algae except (*U.rigida*). No phytane was detected in algae (Clark and Finley 1974). Pristane and phytane have been isolated from petroleum. Trace of phytane was found only in suspect algae sample. It was previously observed in algae samples collected in the polluted area (Clark and Blumer 1967). We found the pristane and phytane in algae tested. Normally phytane was not found in algae. It was exist due to oil pollution in sea. We calculated also Pr (Pristane)/ Ph (Phytane) ratio (Table 12). This ratio is important. When this ratio is higher than 1 it indicates oil pollution. We found this ratio higher than one in *C. barbata, C. fragila, P.squamaria, C. peregrina, Z. prototypes*. Low C18/Ph ratio might indicate the presence of oil degradation.

Branched alkane methyl derivatives of C_9-C_{20}, dimethyl derivates of C_7-C_{12}, C_{17}-C_{20} were detected in algae.

Cyclic hydrocarbons C_5-C_8 derivates and bicyclic hydronaphtalenes were found in some algae. The distributions of these compounds in tested algae were not regular. It was suggested that the origin of these compounds are due to oil pollution.

Saturated aliphatic aldehydes C_6-C_7, C_{10}, C_{12}-C_{18}, and unsaturated aldehydes C_6, C_7, C_8 were identified in algae examined.

Ketones C_6 is detected in algae tested.

Aromatic hydrocarbons have been detected in polluted marine algae (Rosa et al. 1978). We also detected aromatic compound in our earlier work (Güven et al. 1996, Binark et al. 2000). In this work, mono aromatic compounds as benzene derivates, methyl, ethyl, dimethyl, methyl-ethyl, dimethyl-ethyl, trimethyl, tetramethyl diethyl, propyl, butyl, butyl-octyl, butyl-nonyl, hexyl-heptil, C_3 benzene were identified in some algae samples. Their distributions were not regular in algae and depend on the polluted areas.

Aromatic aldehyde, benzaldehyde was found *R.corallicola* and *P. crispa.*
Aromatic substituted alkenes as phenyl methyl propenes were found in *P.nervosa, Z.prototypus, G.verrucosa, C.barbata.* Styrene (ethenyl benzene) were detected in *U.rigida, P.elongata, C.fragile, R.corallina, C.peregrina.*

Aromatic bicyclic hydrocarbons naphthalene derivates (methyl, di/ tri methyl, ethyl) were found in all algae. Indan and its derivates were also detected in some algae. The occurrences of these compounds also depend on the oil pollution.

The important tricyclic aromatic compounds phenanthrene (Phen) was identified in all algae tested. Anthracene (An) was found in *U.rigida, E.muscoides, G. pulchellum, P. elongata, C. mediterranea, C. fragile, P. squamaria, Z. prototypus, G. verrucosa.* An and Phen are isomer compounds. The occurrences of these compounds are due to of oil pollution.

Sulfur containing compounds methyl benzthiophene, benzothiazol and benzothiazolon were detected in some algae.

Other pollutants in algae detected were toxic compounds as phthalates and nonyl phenol.

Phenol, cresols (o-, m-, p-) were found in some algae. The origin of nonyl phenol is the degradation of non ionic surfactant generally present in shampoo.

Phthalates are the main product of the plastifiants. They are found in marine algae (Güven et al. 1997, Gezgin et al. 2001). In this work we detected diethyl, dibutyl, isobutyl, butyl iso butyl phthalates in some algae tested. The origin of this compound is due to pollution of sea.

Kamenarska et al. (2000) investigated volatile compounds in algae collected in the Black Sea. They found aliphatic hydrocarbons, C_{12}-C_{20}, aromatic hydrocarbon benzene derivatives, aliphatic aromatic alcohol, methyl phenol, nonyl phenol, aliphatic, aromatic aldehydes, ketones. Meanwhile erroneously some synthetic compounds as tolbutamide, 4 methyl benzene sulfonamide they identified in algae by GC/MS. These compounds are synthetic products and non volatile compounds. These compounds can not found in marine algae.

Regarding to the abundance peaks on GC/MS chromatograms the Black Sea algae are more polluted than the other examined algae in Dardanelles and Aegean Sea.

Conclusion

Pr/Ph ratio is the parameter of the oil pollution. We found this ratio is higher than one and indicates oil pollution. The homologous series of linear alkyl hydrocarbons were found in algae were found which originated oil pollution.

The examined algae showed a major maximum at n-C_{17} except *U.rigida*. The other differentiation is existence in aromatic compound which is originated from oil pollution. Cycle alkene, aromatic hydrocarbon, alkyl substituted ring compounds, naphteno-aromatic have not yet been reported in marine organism.

Environmental factors cause marked change in oil component distribution in algae. Regarding to GC/MS chromatogram the abundance of peaks the Black Sea is more polluted the other examined sea.

Özet

Bu çalışmada Karadeniz, Çanakkale boğazı ve Ege Deniz'inde toplanan 14 deniz alginin uçucu hidrokarbonları üzerinde inceleme yapılmıştır. Alglerin diklorometan ile ekstrasyonunu takiben distilasyonu sonrası kalan bakiyeye su buharı destilasyonu uygulanmıştır. Böylece uçucu maddeler distilaya alınmıştır. Distilatın eter ile yapılan ekstraksiyonu sonrası ele geçen bakiye GC/MS analizine tabi tutulmuştur. Bu analize ait kromotogramlarda C_9-$C_{22\text{-}27}$ lineer alkil hidrokarbon dizisinde petrolde görülen hidrokarbonlar tespit edilmiştir.

Tayin edilen alifatik bileşikler arasında 19 lineer, 20 dallı, 19 halkalı alkan, 18 alken, 2 alkol, 12 aldehit, 2 keton ve aromatik bileşiklerden 31 tek halkalı, 16 naftalen, 4 indan, 2 adet 3 halkalı ve 3 kükürt içeren maddeler tanımlanmıştır. Buna ek olarak 1 aromatik ve fenil alken derivesi tespit edilmiştir. Pristan/Phytan oranı da tayin edilmiş ve buna dayanarak alkanların petrol kirliliğine ait olduğu ispatlanmıştır.

Bunun yanında Pr/Ph oranının bazı alglerde 1'den küçük olması, ayrıca petrole ait halkalı ve aromatik bileşiklerin tespit edilmesi incelenen alglerin petrol kirliliğine maruz kaldığını göstermiştir. Bu çalışma alglerin deniz kirliliği takibinde bir indikatör olarak kullanılabileceği görüşünü desteklemektedir

GC/MS kromatogramında halkalı bileşiklerin piklerinin abundanslarının yüksekliği bulgularına dayanarak Karadeniz alglerinin Çanakkale ve Ege Denizi alglerinden daha fazla petrol kirliliğine sahip olduğu bulunmuştur. Bu da Karadeniz'in petrolce daha kirli olduğuna işarettir.

Sonuç olarak bu bulgular ve aromatik hidrokarbonların mevcudiyeti alglerin petrol ile kirlendiğini göstermiştir. Ayrıca petrol kirliliğine ait maddelere ek olarak toksik olan ftalat ve nonil fenol alglerde bulunmuştur.

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