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Identification of Phthalate Esters Pollution in the Bosphorus and Dardanelles

İstanbul ve Çanakkale Boğazında Ftalat Esterleri Kirliliğinin Tayini

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Abstract

Pthalate esters are used in various industries. They are toxic for marine organisms and are general contaminants. Phthalate esters were investigated in seawater of the Bosphorus and Dardanelles during 1995 and 1996. The detections were made by using GC/MS analysis and identified phthalate esters were: DEP, BP, DBP and DEHP. The same phthalate esters were found at the entrance and exit of both straits with some variations in months.

Keywords: Phthalate esters, Bosphorus, Dardanelles, seawater

Phthalic acid is a benzene dicarboxylic acid. Its ortho (o-), meta (m-) and para (p-) derivativees are very important for many industries. They are used as alkyd resins, polymeric polyesters, drying/non- drying oils, plasticizers for dyes and fibers etc. The largest amounts of the o-phthalic acid esters are: di methyl (DMP), diethyl (DEP), di-n-butyl (DBP), di (2-ethylhexyl) ester (DEHP), di amyl, diallyl. They are used as plasticizers, parfume fixatives and alcohol denaturants, in preparation of various classes of dyes and intermediates and also as insecticides. m-Derivatives of phthalic acid esters are used in alkydresins, dyes, fibers, sheet, surface coating, film and molding industries. p-Derivative, terephtalic acid esters are used synthetic textiles, polyster films and plasticizing industries.

Industries produce approximately more than billion tonnes of over 25 different phythalete compounds. The increase in utilization of these esters has resulted in widespread contamination of natural and human environment and therefore the concern of investigator has been focussed on the topic. They have been found complexed with the fulvic acid components of humic substances in seawater. Fulvic acid apparently

functions as solubilizer for other insoluble phthalate esters and thus serves to mediate the mobilization, transport and immobilization of these compounds in soil and water.

Phthalate esters were detected in sea water (Giam *et al.*1978; Preston and Al-Omran 1986; Sullivan *et al.*1982; Sullivan *et al.*, 1982; Ernst. 1983; Tan 1995; Waldock 1983) DEHP in surface water ranged from 4.9-130 ng/L, DBP ranged from a nondetectable level to 95 ng/L. The amount of phthalate esters found in sea were fish (3.2 mg/kg) (Stalling *et al.* 1973). in Atolla (Morris, 1970) and shrimp, (Laughlin *et al.*1978)

The toxicity and carcinogenicity of phthalates were discussed by various authors. Phthalic acid causes allergic symptoms in humans. Its anhydride causes corneal burns, from which eyes must be protected. Its odor is found to be disagreable and have a choking effect.

Mutagenecity (Kozumbo *et al.*, 1982), teratogenicity and fetotoxicity (Tomita *et al.*, 1982; Dullingan and Austian, 1973), effect on the reproduction of *Daphnia magma* (Brown and Thompson 1982) physiological disturbance on fresh water amphipod, *Gammarus pulex* (Thuren and Voin, 1991) reduce hatching success from brine shrimp (Giam *et al.*1978).

The first record on the pollution of phthalate in Turkish coasts was the findings of terephthalic acid dimethyl ester (DMT) in the Black Sea algae (Güven *et al.*, 1990).

Thus phthalate esters are recognized as general contaminants of water ecocystems.

Various methods were used for the determinaiton of phthalate esters as: GC (Tan, 1995; Takeshita *et al.*, 1977), GC/MS Sjöberg and Bondenson, 1985); GC/MS (Sherma, 1991; Leung and Giang, 1993; Waldock, 1983 and HPLC (Anon.).

A comprehensive account on the phthalates determination was published by Fichbein and Albro (1972).

This paper reports the pollution of the Bosphorus and Dardanelles seawater by phthalate esters in 1995 and 1996.

Material

Seawater samples were taken at the northern entrance and southern exit of Bosphorus (B1,B2) and Dardanelles (D1,D2) (Fig. 1).

2.8 L seawater sample was taken in brown a bottle and 25 ml dichloromethane (DCM) was added for preservation.

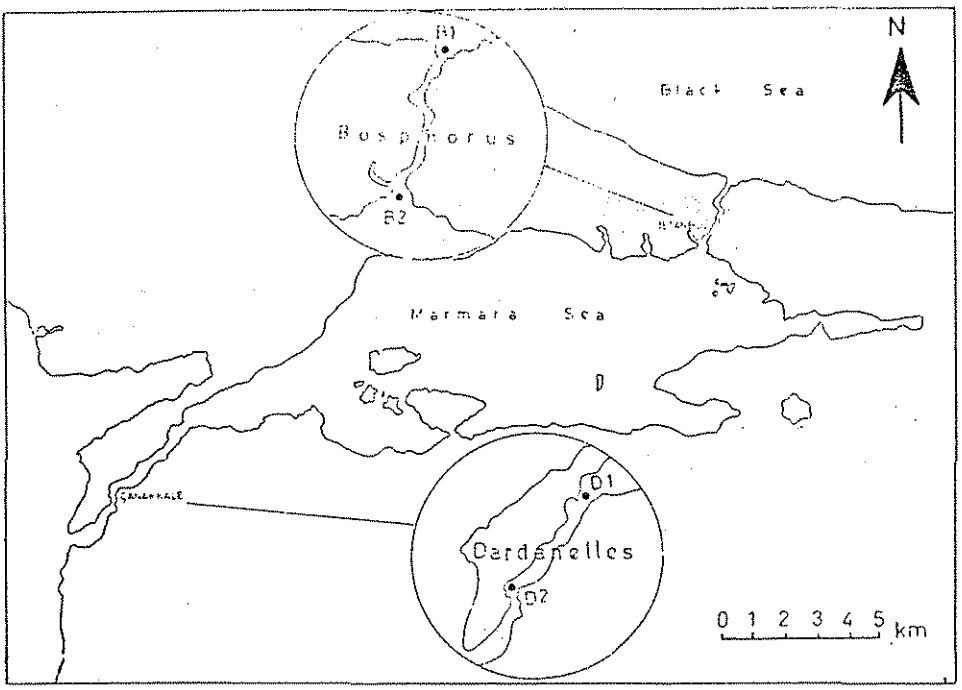

Fig.1 Sampling stations

Methods

1. Seawater

4x700 ml, totaling 2.8L, seawater samples were extracted with 25ml DCM. The extracts were combined and distilled under vacuum. The residue was taken with hexane and analysed by GC/MS.

2. GC-MS analyses

GC/MS analyses were run on a HP 6890 capillary GC connected to a Hewlett Packard Mass Selective Detector (MSD), contolled by a HP Chemstation. Operating conditions were; 50.0 mx0.50μm i.d. fused HP PONA, Methyl siloxane, glass capillary column; oven temperature programme: 40°C at 7 min, from 40-150°C at 15°C min, 150°C at 5 min, from 150-280°C at 15°C min, 280°C at 5 min, from 280-290°C at 10°C min, 290°C at 15 min. Splittless injector temperature 250°C, carrier gas helium, flow 1.0 ml/min, 29.4 psi. press.

Results and Discussion

The detected phthalates in seawater are ; DEP: diethyl phthalate, BP: n-butyl/Isobutyl phthalate, DNP: di-n-butyl phthalate, DEHP: di-ethylhexyl phthalate and tabulated in test stations in Table 1.

GC/MS apparatus was controlled with hexane (HPLC grade) before each test. Thus the mistake on the phthalates that might come from the septum was discarded.

There seems to be no regularity in the presence of phthalates in samples regarding the stations and times indicating that the pollution by phthalates is irregular.

The selected GC/MS chromatograms of examined seawater are shown in Fig.2-6. GC/MS spectra of the samples and the related spectra taken from the memory of the instrument are shown in Fig.7-10.

Some phthalate esters were found at the entrance and exit of both straits, with some variations in months.

The phthalate pollution at 10 m depth of the Bosphorus were found higher than at surface water.

Similar phthalates were found in the southern exit of the Bosphorus as in the northern entrance of the Dardanelles. This fact is considered significant and will be wade a point for further investigation.

It is hereby concluded that the Turkish Straits are also victim of pollution by phthalates as the world seas are in general.

Phthalates	DEP				BP				DNP				DEHP			
Sampling Date / Station	B1	B1	D1	D2	B1	B2	D1	D2	B1	B2	D1	D2	B1	B2	D1	D2
May 1995	-	-	x	x	-	+	x	x	+	+	x	x	+	+	x	x
June 1995	x	x	-	-	x	x	+	+	x	x	+	+	x	x	-	-
Juily 1995	-	-	+	+	+	+	-	-	+	+	+	+	+	+	+	+
Sept. 1995	-	-	x	x	-	-	x	x	-	-	x	x	-	-	x	x
Oct. 1995	-	-	x	x	+	+	x	x	+	+	x	x	+	+	x	x
Dec. 1995	-	-	+	+	-	-	+	+	-	-	+	+	+	-	+	-
April 1996	x	x	-	-	x	x	-	-	x	x	-	-	x	x	-	-
June 1996	x	x	-	-	x	x	+	+	x	x	+	+	x	x	-	-
Agust 1996	x	-	x	x	x	+	x	x	x	+	x	x	x	+	x	x
Oct. 1996	x	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+
Nov. 1996	-	-	-	-	x	+	+	+	x	+	+	+	x	x	-	-
Dec. 1996	-	-	-	-	+	+	+	+	+	+	+	+	-	-	-	x

Table 1. Phthalate pollution of surface water of the Bosphorus and Dardanelles

B1 Northern entrance of the Bosphorus, B2: Southern exit of the Bosphorus

D1: Northern entrance of the Dardanelles, D2: Southern exit of the Dardanelles

DEP: diethyl phthalate, BP: n-butyl/isobutyl phthalate, DNP: di-n-butyl phthalate, DEHP: di-ethylhexyl phthalate

+ : detected, - : Not detected, x : Not tested

Phthalates	DEP				BP				DNP				DEHP			
Sampling Date / Station	B1	B2	D1	D2	B1	B2	D1	D2	B1	B2	D1	D2	B1	B2	D1	D2
July 1995	x	x	+	+	x	x	+	+	x	x	+	+	x	x	+	+
Agust.1995	+	x	x	x	-	x	x	x	-	x	x	x	-	x	x	x
Sept. 1995	x	+	x	x	x	+	x	x	x	+	x	x	x	-	x	x
Oct. 1995	+	x	+	+	-	x	+	+	-	x	+	+	-	x	+	+
Nov. 1995	x	+	x	x	x	+	x	x	x	+	x	x	x	+	x	x
Sept. 1996	x	x	-	-	x	x	-	+	x	x	-	+	x	x	-	+
Oct. 1996	x	x	-	-	x	x	+	+	x	x	+	+	x	x	+	+
Nov. 1996	x	x	-	x	x	x	+	x	x	x	+	x	x	x	+	x

Table 2. Phthalate pollution of on 10 m depth of the Bosphorus and Dardanelles

B1 Northern entrance of the Bosphorus, B2: Southern exit of the Bosphorus

D1: Northern entrance of the Dardanelles, D2: Southern exit of the Dardanelles

DEP: diethyl phthalate, BP: n-butyl/ısobutyl phthalate, DNP: di-n-butyl phthalate, DEHP: di-ethylhexyl phthalate

+ : detected, - : Not detected, x : Not tested

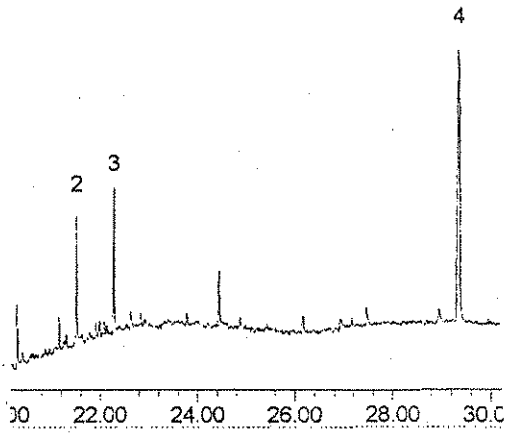

Fig.2. GC/MS chromatogram of B1 station at surface water in 1995.

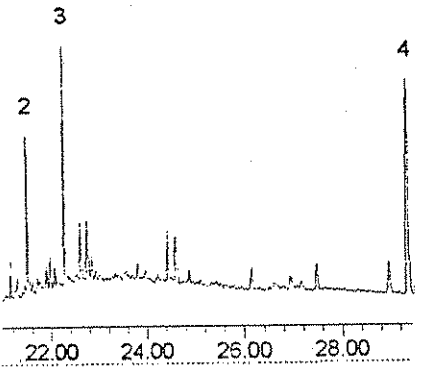

Fig.3. GC/MS chromatogram of B2 station at surface water in 1995.

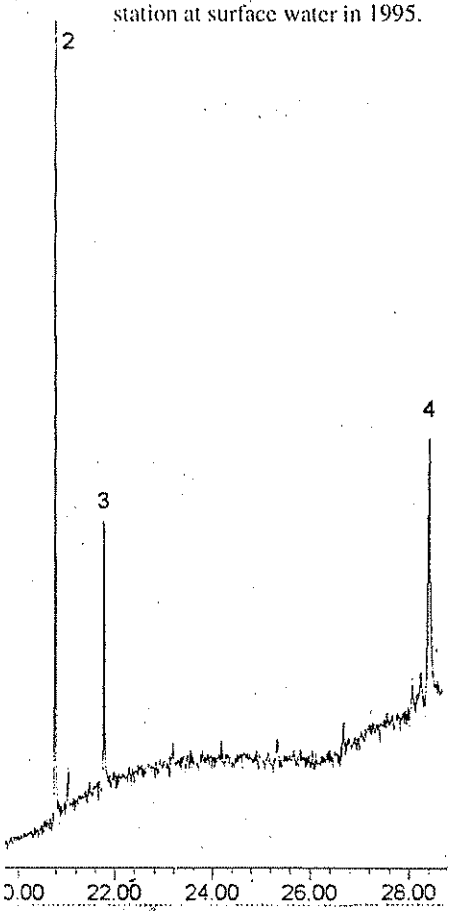

Fig.4. GC/MS chromatogram of B2 station at surface water in 1996.

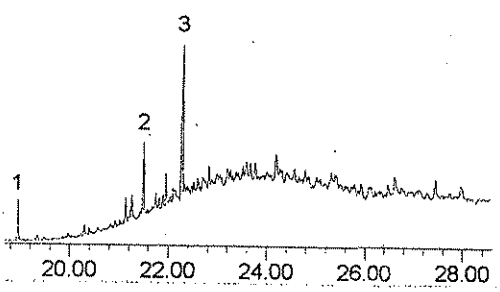

Fig.5. GC/MS chromatogram of D1 station at 10 m depth in 1995.

1-DEP, 2-BP, 3-DNP, 4-DEHP

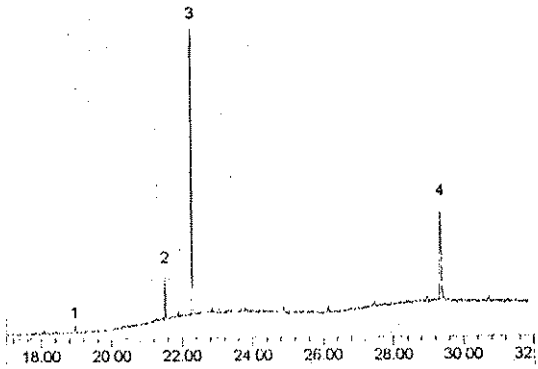

Fig.6. GC/MS chromatogram of D2 station at surface water in 1995.

1-DEP, 2-BP, 3-DNP, 4-DEHP

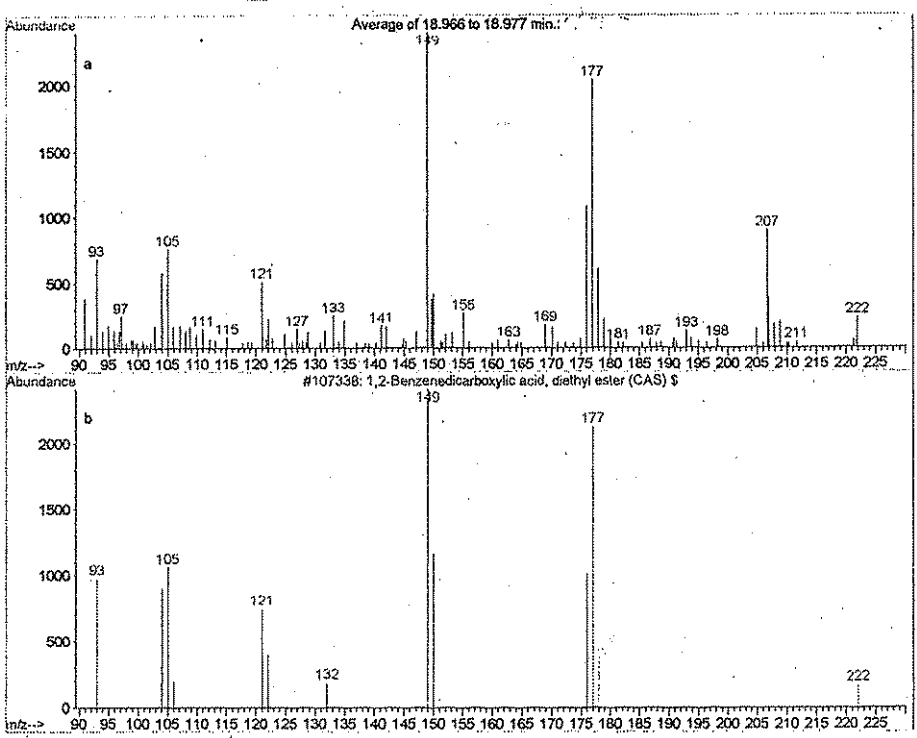

Fig.7. GC/MS spectra of DEP in surface water at station D2.
(a) Spectrum for sample, (b) Spectrum taken from HP memory.

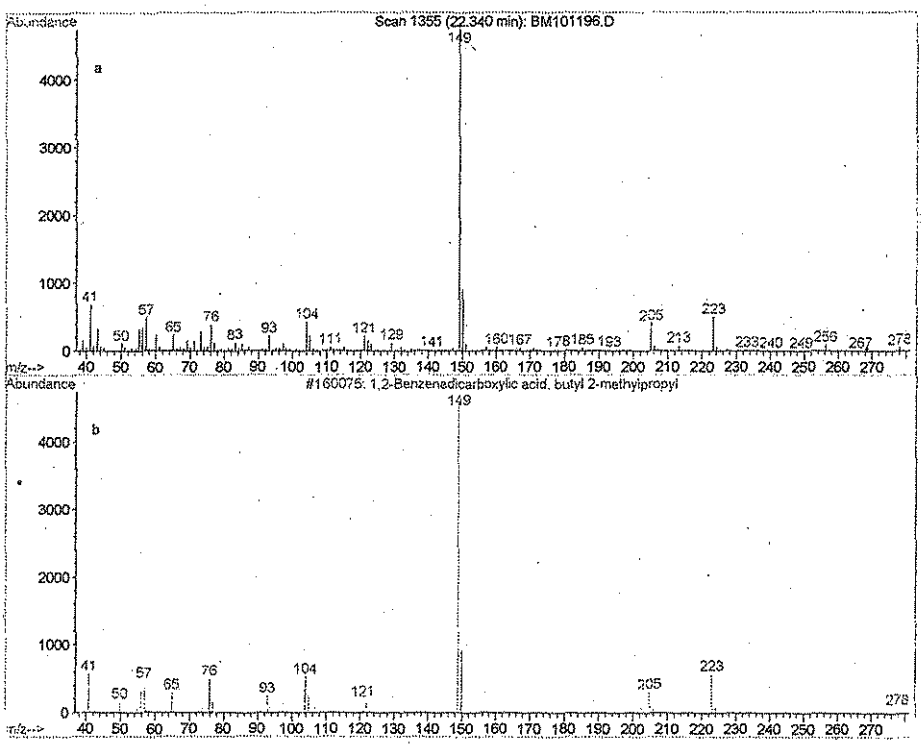

Fig.8. GC/MS spectra of BP in surface water at station B2.
(a) Spectrum for sample, (b) Spectrum taken from HP memory.

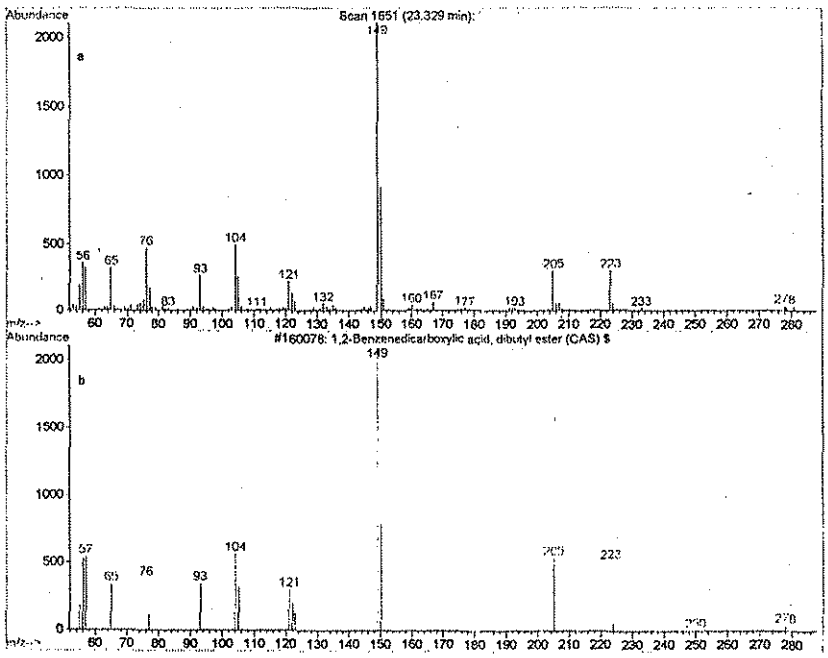

Fig.9. GC/MS spectra of DBP in surface water at station B1.
(a) Spectrum for sample, (b) Spectrum taken from HP memory.

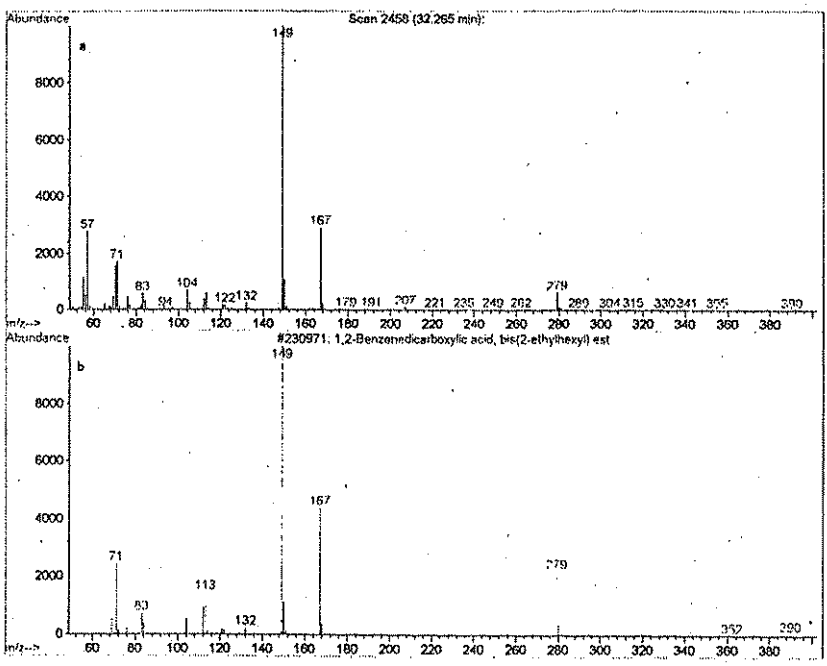

Fig.10. GC/MS spectra of DEHP in surface water at station D1.
(a) Spectrum for sample, (b) Spectrum taken from HP memory.

Özet

Ftalatlar değişik sanayide kullanılan ftalik asit deriveleridir. Bunlar yaygın olarak kullanıldıklarından çevre için kirletici rol oynarlar. Bu maddeler canlılar üzerine değişik toksik etkiye sahiptirler. Bunların deniz suyunda ve canlılarında tespitine ait bir çok yayın vardır. Bu çalışmada 1995-1996 yılında İstanbul Boğazı ve Çanakkale Boğazı deniz suyunda ftalat esterlerinin tespitine ait bulgular verilmiştir. Tayinler GC/MS aletinde yapılmıştır. Tesbit edilen ftalat esterleri : DEP, BP, DBP, DEHP'dir. Farklı aylarda bazı değişmelerle her iki boğazın giriş ve çıkışında aynı ftalat esterlerine rastlanmıştır.

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