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Phthalate esters in marine algae

Deniz alglerinde ftalat esterleri

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Abstract

o-Phthalate esters as diethyl phthalate, dibutyl phthalate, di-isobutyl phthalate and diethylhexyl phthalate were identified at surface and inner part of algae collected in the Bosphorus, as *Ulva lactuca, Enteromorpha linza, Cystoseria barbata, Pterocladia capillaceae* and *Ceramium rubrum*. The same esters were also detected in seawater samples taken from the same area. Thus parallelism in pollution was noted between the algae and the surrounding seawater.

Keywords: Phthalates, algae, Bosphorus.

Introduction

Phthalate esters o- and p- derivatives are used extensively in various industries. They are important pollutants for marine ecosystem. o-Derivative as diethylhexyl phthalate was detected in red algae; *Ceramium rubrum* (Noguchi *et al.*, 1979), dibutyl phthalate, bis isooctyl phthalate, bis isononyl phthalate in brown algae; *Staechospermum marginatum* (Wahidulla and Souza,1995).

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p-Phthalate ester was identified in three red algae, *Acanthophara delilei, Phyllophora nervosa, Hypnea musciformis* (Güven *et.al.*, 1990) . o-Phthalate esters were found in seawater (Waldock, 1983; Tan, 1995; Güven *et.al.*,1997), fish (Stalling *et.al.*1973), jelly fish, Atolla(Morris, 1970), in shrimp (Laughlin *et.al.*, 1978).
This work reports o-phthalate esters in surface and inner part of algae and their relation with the seawater pollution.

Material and method

The algae were collected from the northern entrance and southern exit of the Bosphorus. The sampling sites are shown in Fig. 1. The algae collected were green; *Ulva lactuca* L, *Enteromorpha linza* J. Agard brown; *Cystoseria barbata* J. Agard and red; *Peterocladia capillacea* (Grev) Thuret et Bornet, *Ceramium rubrum* (Huds) J. Agard, from April and May 1995. Reference substances as o-phthalates were obtained from, Diethyl phthalate (DEP) (Fluka) dibutyl phthalate (DBP) (J. Baker) Diethylhexyl phthalate (DEHP) (Plastifay, Turkey). Di-isobutyl phthalate spectrum was taken from Wiley memory.
The solvents used in this study were all HPLC grade (Lab-Scan) and controlled by GC/MS

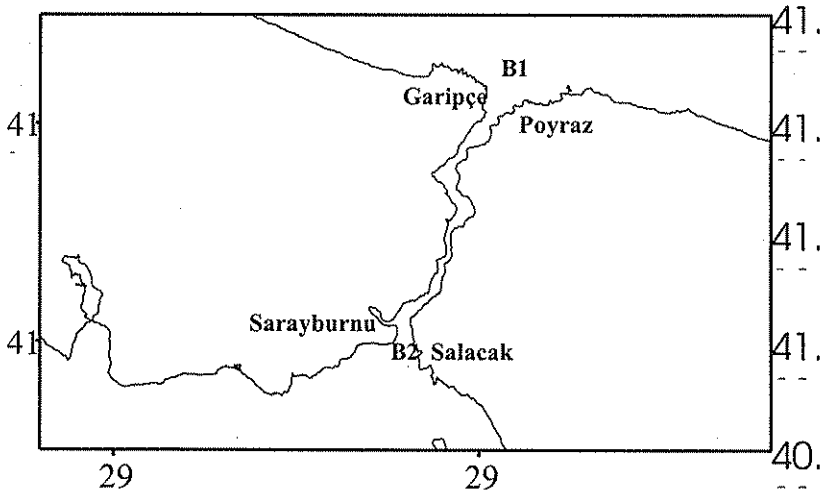

Fig 1. Sampling stations in the Bosphorus

Determination of phthalate

1. On the surface; 100 g algae (wet weight) was rinsed with 3x50 ml dichloromethane (DCM) (Lab-Scan), then filtrated through a filter paper.
The residue was separated (a) and the filtrate was dried over anhydrous Na_2SO_4 , re-filtered and distilled under vacum. The residue was taken with hexane (Lab-Scan) and analysed by GC/MS.
2. Inside of algae; The separated algae (a) material as described above was dried in open air and milled, then extracted with DCM in Soxhlet for 4 h. The organic phase was separated, dried over anhydrous Na_2SO_4 then distilled under vacum. The residue was taken with hexane and analysed GC/MS.

Analyses by GC/MS

The GC/MS analysis was made by HP 6890 capillary GC connected to a Hewlett Packard Mass Selective Detector (MSD) controlled by HP ChemStation. Operating conditions were: 50 m x 0.20 mm fused HP PONO, methyl siloxane, glass capillary column; oven temperature programme; 40 ^{0}C at 6 min., from 40-280 ^{0}C at 10 ^{0}C/min., 280 ^{0}C at 10 min, from 280-290 ^{0}C at 10 ^{0}C/min., at 5 min.; spiltless injector temperature 300 ^{0}C ;carrier gas Helium.
The reference subtances were used in a concentration of 0.1 µg/ml in hexane, the detection was made by GC/MS chromatograms

Results

Four phthalates as diethyl phthalate, dibuthyl phthalate,diisobuthyl phthalate and diethylhexyl phthalate were detected in the surface and inner part of the algae as *Ulva lactuca, Enteromorpha linza, Cystoseria barbata, Pterocladia capillaceae* and *Ceramium rubrum.* The phthalates identified are listed in Table 1 and their chromatogram are shown in Fig. 2-5
GC/MS spectral data obtained from algal extract those, from the authentic compounds and also that taken from the HP ChemStation Fig. 6-9 are the same.

The mass spectral data are: 170eV,m/z (rel.int)

DEP : 222$[M]^+$, 177, 149, 121, 105, 93, 76, 65, 50
DBP : 278$[M]^+$, 223, 205, 149, 121, 104, 93, 76, 65, 50
DIBP: 278$[M]^+$, 167, 149, 104, 93, 76, 57, 41
DEHP : 390$[M]^+$, 362, 279, 167, 149, 132, 113, 83,71

Retention times (min) are ;DEP;16.372, DBP;21.248, DIBP;22.918, DEHP;31.501.

The same phthalates were detected on surface and inner part of algae collected at the northern entrance and southern exit of the Bosphorus in April and May 1995. Similar results were obtained for seawater at the same area.

DEP was found only in surface of *P. capillacea;* It was also found in the some sample of seawater taken from the entrance and exit of Bosphorus in 1995 .

The origin of o-phthalates in algae is unknown , but certainly they must have been taken from the aquatic environment . Güven *et al.* (1990) demonstrated that accumulation of p-derivative of phthalates depended on the sea pollution. The existence of o-phthalate esters on the surface and inner part of algae proved that the algae were polluted by the surrounding water.

Generally, the pollution has been published regarding the total algae whereas in our work the phthalate absorption on surface and adsorption internally were identified separately.

This finding also supported the importance of using algae as an indicator of seawater pollution.

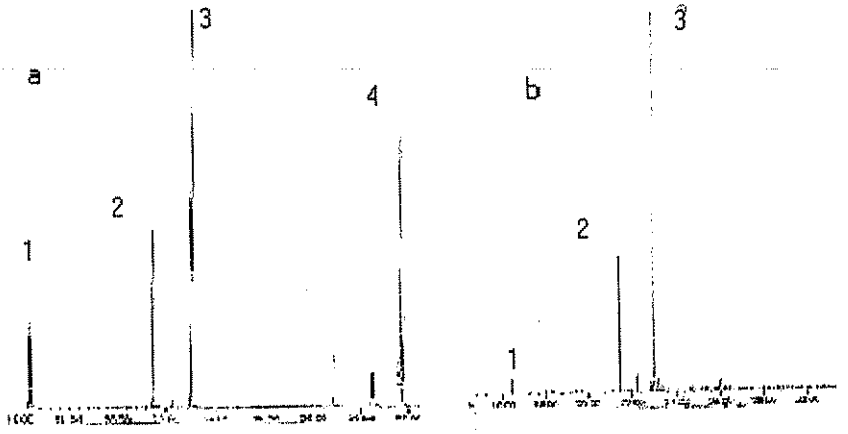

Fig.2. The chromatogram of *Ulva lactuca,* Salacak
a) Surface b) Inner part
1. DEP 2. DİBP 3. DBP 4. DEHP

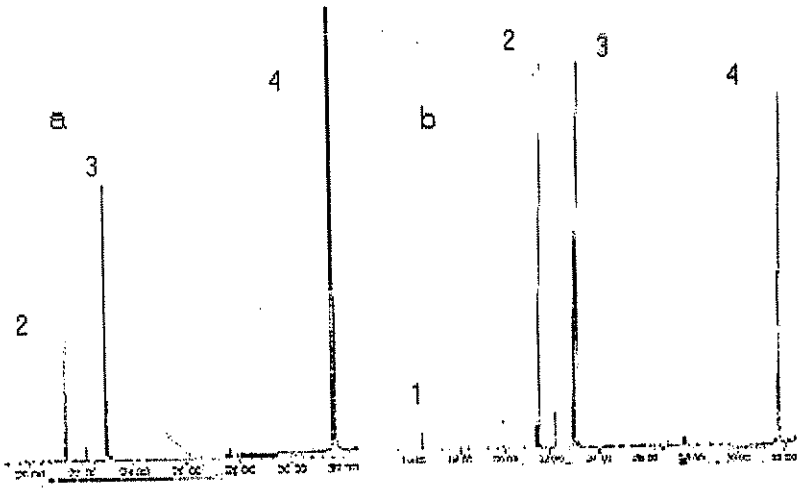

Fig.3. The chromatogram of *Enteromorpha linza,* Sarayburnu
a) Surface b) Inner part
1. DEP 2. DİBP 3. DBP 4. DEHP

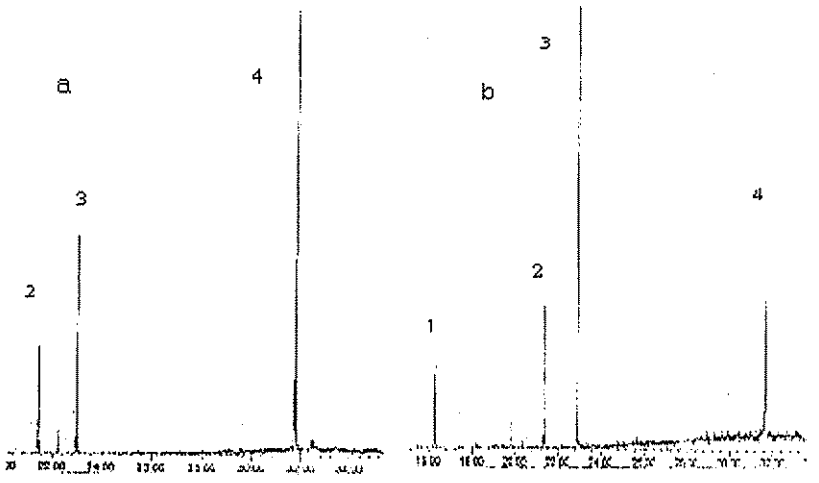

Fig.4. The chromatogram of *Cystoseira crinata,* Garipce
b) Surface b) Inner part
1. DEP 2. DİBP 3. DBP 4. DEHP

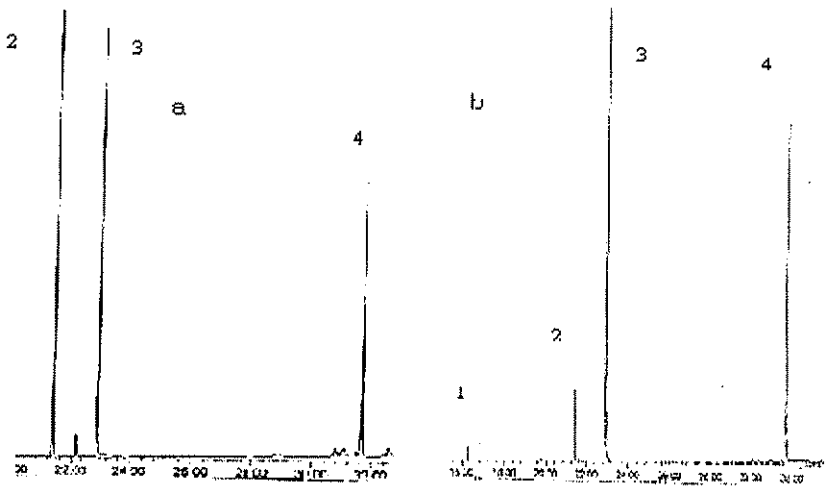

Fig.5. The chromatogram of *Enteromorpha linza,* Poyraz
a) Surface b) Inner part
1. DEP 2. DİBP 3. DBP 4. DEHP

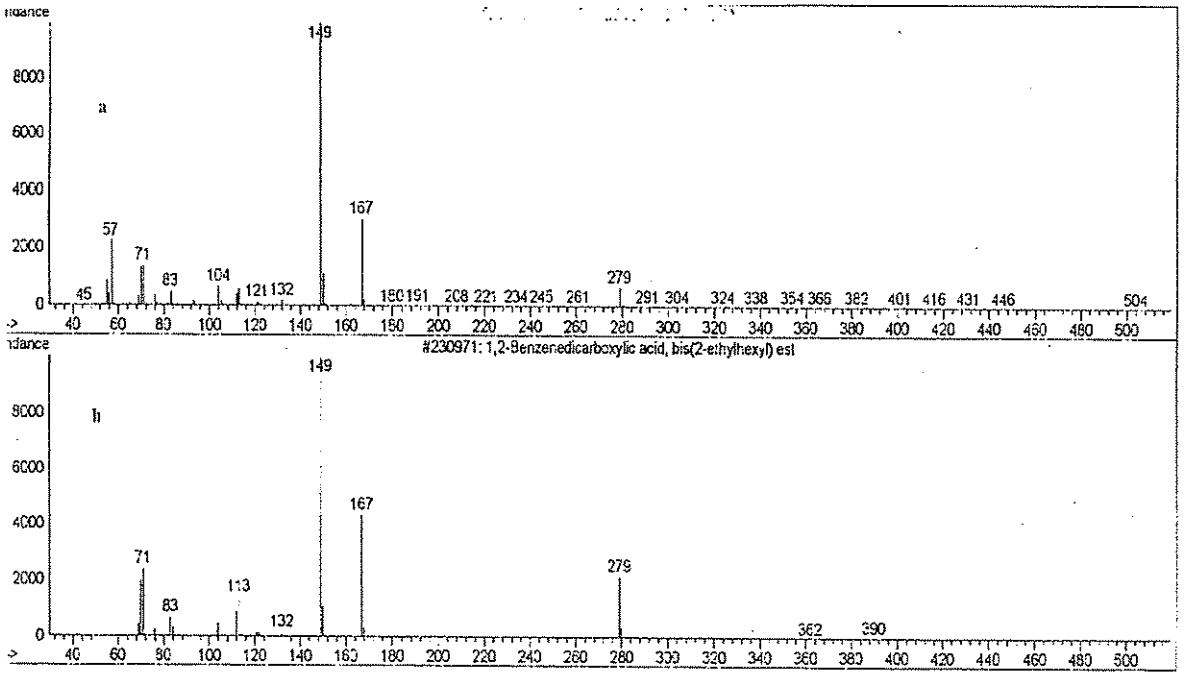

Fig.6. Diethylhexyl phthalate spectrum
a) Sample b) Taken from Wiley library memory

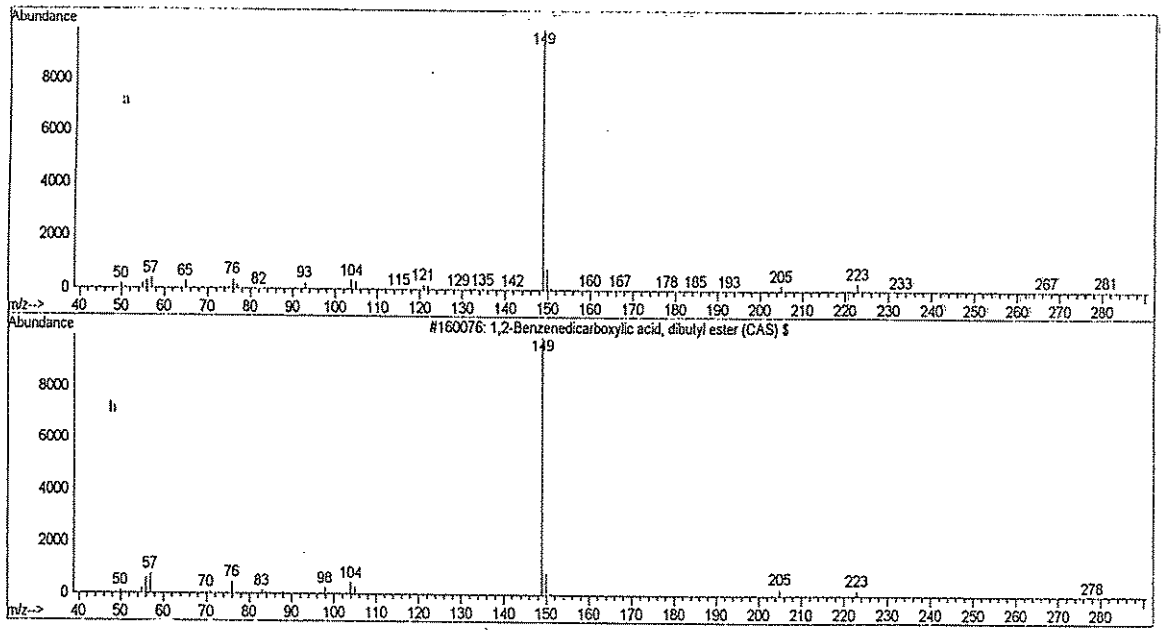

Fig.7. Dibutyl phthalate spectrum
a) Sample b) Taken from Wiley library memory

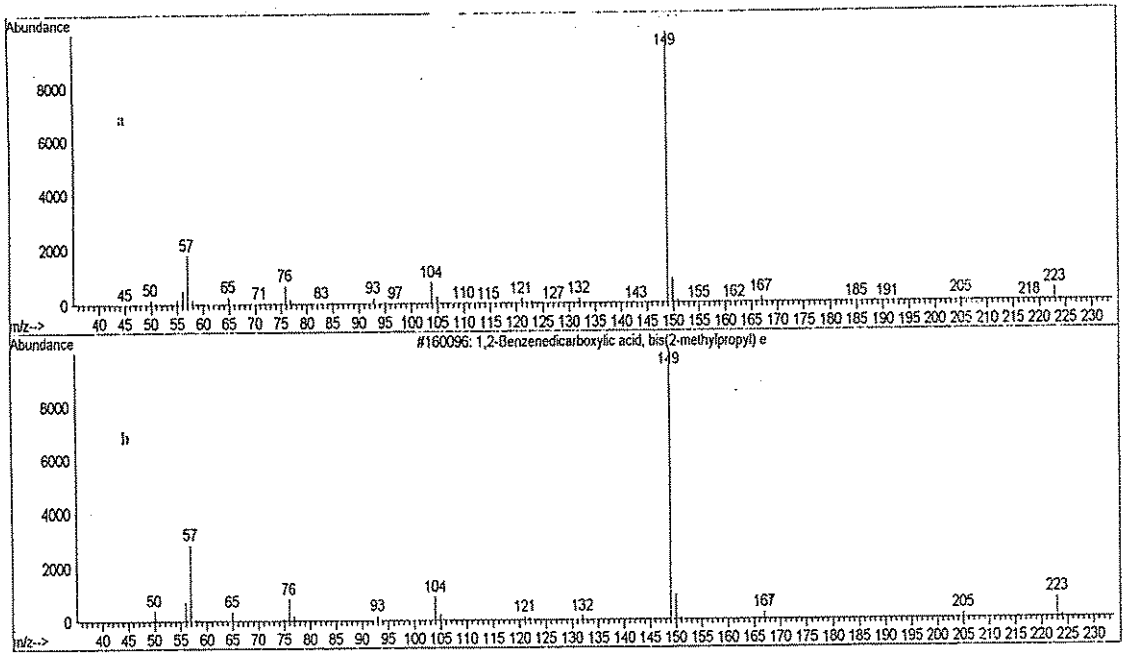

Fig.8. Diisobutyl phthalate spectrum
a) Sample b) Taken from Wiley library memory

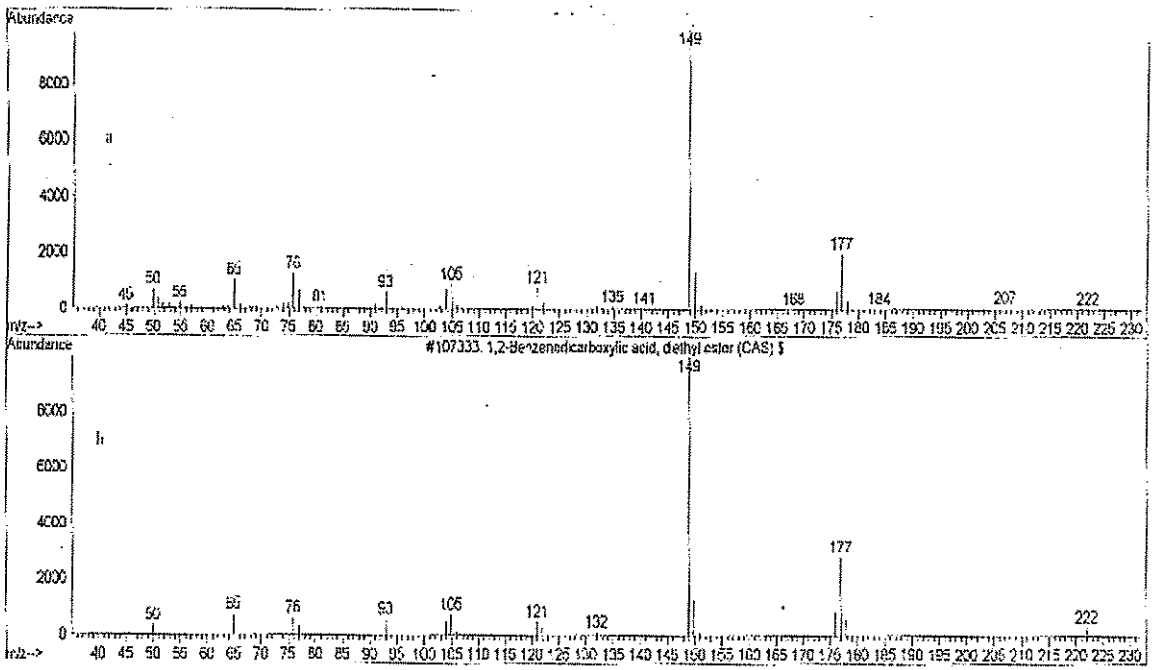

Fig.9. Diethyl phthalate spectrum
a) Sample b) Taken from Wiley library memory

Table 1. Phthalates content on surface and inner part of algae collected from the Bosphorus in April and May , 1995.

	Ulva lactuca				*Enteromorpha linza*				*Cystoseira barbata*				*Pterocladia capillacea*				*Ceramium rubrum*			
	Surface		Inner part		Surface		Inner part		Surface		Inner part		Surface		Inner part		Surface		Inner part	
	1	2,3,4	1	2,3,4	1	2,3,4	1	2,3,4	1	2,3,4	1	2,3,4	1	2,3,4	1	2,3,4	1	2,3,4	1	2,3,4
Garipçe	-	+	+	+	-	+	+	+	+	+	-	+	+	+	+	+	-	+	-	+
Poyraz	-	+	-	+	-	+	-	+	+	+	-	+	-	+	-	+	-	+	-	+
Saraybu rnu	-	+	-	+	-	+	+	+	x	+	-	+	+	+	-	+	-	+	+	+
Salacak	-	+	+	+	-	+	+	+	+	+	-	+	x	+	x	+	-	+	-	+

+ : detected, - : not detected, x : the alga was not found in this area. phthalates: 1: Diethyl phthalate, 2: Dibutyl phthalate, 3: Di-iso-butyl phthalate, 4: Diethylhexyl phthalate

Özet

o-Ftalat esterleri dietil ftalat,dibutil ftalat, di-isobutil ftalat ve dietilhekzil ftalatları İstanbul Boğazı girişi ve çıkışından alınan *Ulva lactuca, Enteromorpha linza, Cystoseira barbata, Pterocladia capillaceae* ve *Ceramium rubrum* alglerinde tespit edilmiştir. Benzer esterler aynı bölgeden alınan deniz suyu numunelerinde de rastlanmıştır. Bu şekilde alg ve deniz suyunda ftalat kirliliği arasında paralellik tespit edilmiştir.

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