

## RESEARCH ARTICLE

### Phthalates pollution in algae of Turkish coast

**Sinem Erakın, Neşe Binark, Kasım Cemal Güven<sup>1\*</sup>, Burak Coban<sup>2</sup>,  
Hüseyin Erduğan<sup>3</sup>**

<sup>1</sup> Turkish Marine Research Foundation (TUDAV), P. O. Box: 10, Beykoz, Istanbul, TURKEY

<sup>2</sup> Department of Chemistry, Faculty of Arts and Sciences, Bulent Ecevit University, Zonguldak, TURKEY

<sup>3</sup> Department of Biology, Faculty of Science, 18 Mart University, Çanakkale, TURKEY

\*Corresponding author: [kcguyen@yahoo.com.tr](mailto:kcguyen@yahoo.com.tr)

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#### Abstract

In this work phthalates pollution in red, brown and green algae in the Black Sea, Istanbul Strait and Çanakkale Strait were investigated. The detected phthalate derivatives were DEP, DIBP, DBP and DEHP. Very toxic phthalate DEHP was found only in the Istanbul Strait. Phthalates pollution of algae depends on the pollution of sea water.

**Keywords:** Phthalates, red, brown, green algae, Turkish coast

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#### Introduction

Phthalates are phthalic acid esters used since 1931. They increase flexibility and transparency of plastics, detergents, wax, paints, printings, textiles and also used in pharmacy as tablet coatings, emulsifying, suspending agents and cosmetics. They were used approximately six million tons every year. Phthalates are released into environment during various utilization and create high risk for human health. They cause breast/hepatic cancer, allergies, disrupt endocrine system. Various phthalate derivatives are shown in Table 1.

Phthalates have been detected in seawater and marine organisms by various authors (Giam *et al.* 1978; Sullivan *et al.* 1982; Ernst 1983; Waldock 1983; Preston and Al-Omran 1986; Tan 1995; Wahidulla and De Souza 1995), in fish (Stalling *et al.* 1973), in jellyfish in the atoll (Morris 1970), in shrimp (Laughlin *et al.* 1978).

Toxicity of phthalates for marine organisms such as algae increases risk for human health through bioaccumulation (Adams *et al.* 1995; Staples 1997).

**Table 1.** Phthalate derivatives, abbreviation, and formulas

Phthalate derivative	Abbreviation	Formula
Dimethyl phthalate	DMP	$C_6H_4(COOCH_3)_2$
Diethyl phthalate	DEP	$C_6H_4(COOC_2H_5)_2$
Di- <i>n</i> -propyl phthalate	DPP	$C_6H_4[COO(CH_2)_2CH_3]_2$
Di- <i>n</i> -butyl phthalate	DBP	$C_6H_4[COO(CH_2)_3CH_3]_2$
Diisobutyl phthalate	DIBP	$C_6H_4[COOCH_2CH(CH_3)_2]_2$
Butyl isobutyl phthalate	BIBP	$C_6H_4[COOCH_2CH(CH_3)_2][COO(CH_2)_3CH_3]$
Di- <i>n</i> -hexyl phthalate	DNHP	$C_6H_4[COO(CH_2)_5CH_3]_2$
Diisohexyl phthalate	DIHxP	$C_6H_4[COO(CH_2)_3CH(CH_3)_2]_2$
Di-2-ethylhexyl phthalate	DEHP	$C_6H_4[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]_2$
Di- <i>n</i> -octyl phthalate	DNOP	$C_6H_4[COO(CH_2)_7CH_3]_2$
Diisooctyl phthalate	DIOP	$C_6H_4[COO(CH_2)_5CH(CH_3)_2]_2$

Phthalates have been found in various samples collected in the Turkish environment: in Taşkoprü stream, İzmit (Güven *et al.* 1997), sea water (Güven *et al.* 1997; 2003), in Golden Horn (Cumalı and Güven 2008), in fish (Güven and Coban 2013), in mussels (Güven *et al.* 2003), in algae (Güven *et al.* 1990; Gezgin *et al.* 2001; Gezgin *et al.* 2001; Erakın and Güven 2008).

In this paper, we report the phthalate esters in red, brown and green algae collected from the Black Sea, Istanbul Strait (Bosphorus), and Çanakkale Strait (Dardanelles) and Aegean Sea.

## Materials and Methods

*Algae:* The algae samples were collected in January 2005 from the Black Sea and the Çanakkale Strait, in Dec 1995 from the Istanbul Strait except *Gracilaria verrucosa* in 2002, Izmir, the Aegean Sea. The samples collected are shown in Table 2.

*Extraction:* 60 g powdered algae sample were mixed with 20 g anhydrous sodium sulfate and extracted with dichloromethane in a Soxhlet apparatus for 8 h, the extract was distilled at 40 °C. The residue was taken with hexane then applied to GC/MS apparatus.

*GC-MS analysis:* HP 6890 capillary GC equipped with a split/splitless injector was used (splitless time 1 min, flow rate 1 ml min<sup>-1</sup>, 29.4 psi. press.), the injector temperature was maintained at 240°C. The GC temperature was programmed as from 50°C (2 min) to 290°C (15 min) at 5°C (1 min). The capillary column used was PONO (HP) 60 m x 0.25 mm x 0.25 µm. The GC was coupled to an HP 5972 Mass Selective Detector. The mass spectrometer was operated under the selective ion monitoring mode and the signal was acquired on the molecule ion of the studied components (Electron impact at 70 eV, 2000 V, 1.4 scans s<sup>-1</sup>, and dwell time 40 ms). The interference temperature

was 290°C. The volatile compounds in algal extract were identified by comparing the retention time and its spectrum with HP memory and our earlier work. Solvents used were Merck and chemical La Chemia products.

**Table 2.** Collection sites and divisions of algae

Station	Division	Algae
Şile (TBlack Sea)	Chlorophyta	<i>Ulva rigida</i> C. Agardh
		<i>Enteromorpha muscoides</i> (Clemente) Cremades <i>Enteromorpha linza</i> (Linnaeus) J. Agardh
	Rhodophyta	<i>Gelidium pulchellum</i> (Turner) Kützing <i>Polysiphonia elongata</i> (Hudson) Sprengel <i>Corallina mediterranea</i> Ellis & Solander
Istanbul Strait	Phaeophyta	<i>Cystoseira barbata</i> (Stackhouse) C. Agardh
	Chlorophyta	<i>Ulva lactuca</i> L. <i>Enteromorpha linza</i>
	Rhodophyta	<i>Ceramium rubrum</i> (Huds.) J. Agardh <i>Pterocladia capillacea</i> (Grev.) Thuret et Bornet <i>Gelidium pulchellum</i> var. <i>claviferum</i>
Çanakkale Strait	Phaeophyta	<i>Cystoseira barbata</i> J. Agardh
	Chlorophyta	<i>Codium fragile</i> (Suringar) Hariot
	Rhodophyta	<i>Peyssonnelia squamaria</i> (S. S.Gmelin) Decaisne <i>Rhodymenia corallina</i> Ardissonne <i>Phyllophora nervosa</i> (A.P. de Candolle) Greville
	Phaeophyta	<i>Cystoseira barbata</i> (Stackhouse) C. Agardh <i>Colpomenia peregrina</i> Sauvageau <i>Zanardinia prototypus</i> (Nardo) Nardo
Izmir (Aegean Sea)	Rhodophyta	<i>Gracillaria verrucosa</i> (Hudson) Papenfuss

## Results and Discussion

The phthalate esters found in algae (Collection site in parenthesis) were:

### Rhodophyta

*Gracilaria verrucosa*: DBP (Izmir)

*Polysiphonia elongata*: DIBP (Şile, Black Sea)

*Phyllophora nervosa*: DIBP, DBP (Şile, Black Sea)

*Rhodymenia corallina* var. *spathulata*: DIBP (Şile, Black Sea)

*Ceramium rubrum* (Huds.) J. Agardh: DBP, DIBP, **DEHP** (Garipce, Salacak, Istanbul Strait)

*Gelidium pulchellum* var. *claviferum*: DIBP, DBP, **DEHP** (Anadolu Feneri, Istanbul Strait)

### Phaeophyta

*Cystoseira barbata*: DBP, DIBP, DEP, **DEHP** (Anadolu Feneri and Garipce, Salacak, Istanbul Strait)

*Zanardinia prototypus*: DBP, DIBP (Çanakkale Strait)

*Colpomenia peregrina*: DBP, DIBP (Çanakkale Strait)

## **Chlorophyta**

*Ulva rigida*: DIBP (Şile, Black Sea)

*Ulva lactuca* L.: DBP, **DEHP** (Garipce, Anadolu Feneri, Salacak, İstanbul Strait)

*Enteromorpha muscoides*: DBP (Şile)

*Enteromorpha linza*: DEP, DIBP, DBP, **DEHP** (Salacak, İstanbul Strait)

We found various phthalates in the examined algae. These findings show that phthalates pollution of algae depends on the pollution of the collection sites.

## **Türkiye sahillerindeki alglerde ftalat kirliliği üzerinde çalışmalar**

### **Özet**

Bu çalışmada Karadeniz, Çanakkale Boğazı ve Ege Deniz'inden toplanan 15 alg üzerinde ftalat kirliliği sonuçları verilmiştir. Tespit edilen ftalat derivelere; DEP, DBP, DIBP, DEHP'tir. Ftalatların alglerdeki kirliliğinin sebebi deniz kirliliğine bağlıdır. Ftalatlar arasında en zehirli olan DEHP'ye sadece İstanbul Boğazı'ndaki değişik alglerde rastlanmıştır.

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