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RESEARCH ARTICLE

Phthalate pollution in fish *Sarda sarda*, *Engraulis encrasicolus*, *Mullus surmuletus, Merlangius merlangus* and shrimp *Parapenaeus longirostris*

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Abstract

Phthalate esters pollution was investigated in fish *Sarda sarda, Engraulis encrasicolus*, *Mullus surmuletus,* and *Merlangius merlangus* from the Black Sea and shrimp *Parapenaeus longirostris* from the Sea of Marmara. The identified phthalate esters were dioctylphthalate in flesh and dibutylphthalate in digestive tract of *E. encrasicolus* and isobutylphthalate in digestive tract of *S. sarda* and *M. surmuletus*. However, phthalate derivatives were not found in *M. merlangus* and *P. longirostris*. This is the first record for phthalates found in fish and shrimp in Turkish coasts.

Key words: GC/MS, Phthalates, fish.

Introduction

Phthalate esters are *o*- and *p*-dicarboxylic acid esters of benzenes. Diethylphthalate (DEP), butylphthalate (BP), dibutylphthalate (DBP) and diethylhexylphthalate (DEHP) are extensively used in various industries for variety of purposes as alkylated resins, polymeric polyesters, drying or non-drying oils, plasticizers, insecticides, fibers, perfume fixative, alcohol denaturant, surface coating agents, molding industries, and *p*- derivatives, terephthalic acid esters are used in synthetic textile industry. The annual productions of phthalates are over 25 billion tones.

Phthalate esters were detected in seawater 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) and also in the seawater in Golden Horn (Cumalı and Guven 2008).

Phthalate esters were detected in marine organisms as contaminants in fish (Stalling *et al.* 1973), in jellyfish in the atoll (Morris 1970), in shrimp (Laughlin *et al.* 1978) in mussel, DEHP, DP, diisobutylphthalate were detected in the Dardanelles (Guven *et al.* 2003). In algae, orthophthalate esters were detected in Istanbul Strait (Gezgin and Guven 2001), in the Black Sea and Dardanelles (Erakın and Guven 2008). *p*-Phthalate ester was identified in the Black Sea coastal algae (Guven *et al.* 1990).

The toxicity and carcinogenicity of phthalate esters were studied by various authors (Adams *et al*. 1995; Huang *et al.* 1999; Benson 2009). Mutagenecity (Kazumba *et al.* 1982), teratogenecity and fetotoxicity (Dulligan and Austian 1973; Tomita *et al*. 1982), effect on the reproduction of *Daphnia magma* (Brown and Thompson 1982), physiological disturbance on fresh water amphioid, *Gammarux pulex* (Thuren and Voin 1991), reduction of hatching success from brine shrimp (Giam *et al.* 1978) have been reported. Natural mixed algae showed decreasing cell density and species number after they were exposed to DBP (Kuang *et al.* 2003).

Materials and Methods

The Black Sea fish species *Sarda sarda* (Bloch 1783), *Merlangius merlangus* (L. 1758*)*, *Mullus surmuletus* (L. 1758), *Engraulis encrasicolus* (L. 1758) and shrimp sample *Parapenaeus longirostris* (Lucas 1846) taken from the Sea of Marmara were purchased from the fish market in Kumkapı, Istanbul in 2005.

The examined samples (50 g) were freeze-dried and extracted with 150 ml dichloromethane in Soxhlet apparatus and processed as described in previous work (Guven *et al*. 2003). The residue was taken with 2 ml hexane and applied to GC-MS.

GC-MS analysis: HP 6890 capillary GC equipped with a split/splitless injector was used (splitless time 1 min, flow rate 1 ml min^{-1}, 29.4 psi. press.), the injector temperature was maintained at 240 ^{o}C. The GC temperature was programmed as from 50 ^{o}C (2 min) to 290 ^{o}C (15 min) at 5 ^{o}C min^{-1}. 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^{-1}, dwell time 40 ms). The interference temperature was 290 ^{o}C.

Identification of the phthalate derivatives was based on the comparison of its mass spectra with mass spectral data from literature (Gezgin and Guven 2001).

Results and Discussion

As seen in Table 1 the phthalate derivatives were found as: dioctylphthalate in flesh of *E. encrasicolus*, diisobutylphthalate in digestive tract of *S. sarda* and *M. surmuletus* and dibutylphthalate in digestive tract of *E. encrasicolus* but phthalate derivatives were not found in fish *M. merlangus* and shrimp *P. longirostris*. These pollutants were found earlier in mussel collected from Dardanelles (Guven *et al.* 2003). Phthalates are important problem and dominant pollutant for environment in all seas. They are toxic compounds for human health and they should be screened regularly but there is no international limit value. It is necessary to propose a limit value for this purpose.

This is the first report for phthalates in fish taken from the Turkish coasts.

Table 1. The phthalate derivatives found in fish

Phthalates	*S. sarda*		*E. encrasicolus*		*M. surmuletus*	
	Flesh	Digest. tract	Flesh	Digest. tract	Flesh	Digest. tract
Dioctylphthalate	-	-	+	-	-	-
Diisobutylphthalate	-	+	-	-	-	+
Dibutylphthalate	-	-	-	+	-	-

- not detected.

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Palamut, hamsi, tekir, mezgit baklıkları ile karideste ftalat kirliliği araştırması

Özet

Bu çalışmada Kumkapı Balık Hali'nden alınan *Sarda sarda*, *Engraulis encrasicolus*, *Mullus surmuletus, Merlangius merlangus* ve *Parapenaeus longirostris* türlerinde ftalat kirliliği araştırılmıştır. Bunun sonucunda ftalat esterlerinden dioktilftalatın hamsinin etli kısmında, dibutilftalatın hamsinin sindirim sisteminde ve diisobutilftalat palamutun ve tekirin sindirim sisteminde bulunduğu tespit edilmiştir. Mezgitte ve karideste ise ftalat bulunmamıştır. Bu çalışma Türkiye sahillerindeki deniz balıklarında ve karideste yapılan ilk çalışmadır. Daha evvelce yaptığımız çalışmada ise ftalat esterleri midyede ve deniz alglerinde tespit edilmişti. Ftalat esterleri çok geniş olarak sanayide kullanıldığından çevreyi kirleticiler arasında önemli bir yeri vardır. Bütün organizmalar için toksik etkisi vardır, fakat herhangi bir limit değer verilmemiştir. Bu konuda limit değeri üzerine çalışmalar yapılmalıdır.

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