RESEARCH PAPER

The pollution of 3-nitrophthalic acid in the sea water of the Aegean Sea and mussels collected from the Çanakkale Strait (Dardanelles) and 3-nitrostyrene in the sea water of the Golden Horn, Istanbul

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Abstract

3-nitrophthalic acid was detected in the water of the Aegean Sea and in the mussels collected from the Çanakkale Strait (Dardanelles). 3-nitrostyrene was detected in the sea water of the Golden Horn, Istanbul. The detection of 3-nitrophthalic acid in mussels and 3-nitrostyrene in sea water was made for the first time in aquatic environment.

Keywords: 3-nitrophthalic acid, 3-nitrostyrene, Golden Horn, Aegean Sea, mussel, GC/MS analysis

Introduction

3-Nitrophthalic acid (Figure 1a) was prepared by the nitration of phthalic acid (Miller 1881; Culhane and Woodward 1927). Various nitro aromatic compounds were detected in diesel and gasoline exhaust. These were products of burning fuel and airborne nitrogen oxides (NOx). It is the main pollutant of urban air. It is produced by conversion of nitrogen monoxide originated from vehicles (Lee 2005) and also ships (Ijlstra 1990). It gives several nitro compounds such as 1-nitropyrene (Samanta et al. 2002), 1,3-dinitropyrene and 1,8-dinitropyrene, nitro- and dinitro-PAH (Pohjola 2004). 3-Nitrophthalic acid was at first detected in the sea water of Golden Horn, Istanbul by the side of a boat (Cumali and Güven 2007).

These nitro compounds are carcinogenic/mutagenic for human (Wesp et al. 2000; Hansen et al. 2004; Pohjola et al. 2004). In this work, these compounds in
the sea water of the Golden Horn and Aegean Sea and the mussels collected from the Çanakkale Strait (Dardanelles) were reported. Hayakawa et al. (1995) reported that automobiles are the main source of atmospheric PAH’s and nitro-PAH’s.

Figure 1. Detected compounds a) 3-nitrophthalic acid; b) 3-nitrostyrene; and c) Sampling stations (Knidos, Çanakkale Strait (Dardanelles) and Golden Horn).

**Materials and Methods**

The sampling stations were Knidos (26°30′50″N 27°22′01″E), Çanakkale Strait (Dardanelles) and Golden Horn Bridge (Figure 1c). The sea water samples were collected in April 2005 and mussel samples are collected in March 2002.

*Extraction:*
800 ml sea water was extracted three times with Dichloromethane (DCM) the extract was distilled, residue was taken with hexane and applied to GC/MS for analysis.

40 g mussel samples were mixed with anhydrous sodium sulfate and extracted for 8 h in a soxhlet apparatus. The extract was filtered and dried over anhydrous sodium sulfate then distilled at 40°C, the residue was saponified with 5 ml 5% potassium hydroxide in ethanol by heating for 2h under reflux in water bath, 50 ml of water was added and extracted with 50 ml pentane. The organic phase was distilled and applied to GC/MS for analysis.
GC/MS analysis: The instrument used is a gas chromatography-mass spectrometer (HP6890 Series GC System; Hewlett Packard, Wilmington, DE, USA) fitted with an electronic pressure control and mass selective detector (HP5972A with ionization energy, 70 eV; source temperature, 280°C) using a HP-5MS capillary column (30 m x 0.25 mm i.d., 0.25 µm film thickness). The chromatographic conditions were as follow: 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 the carrier gas (1 ml/min).

The oil components were identified by the comparison of the mass spectra of the samples with spectra of HP memory.

Chemicals: Reference compound of 3-nitrophthalic acid was purchased from Acros Organic (Belgium). Solvent: Dichloromethane (HPLC grade Lab Scan, Ireland). Hexane (Merck, Germany).

Results

As the GC/MS chromatogram is shown in Figures 2 and 3, 3-nitrophthalic acid was detected (Rt: 28.60-28.86) in sea water collected from an exhaust area of a boat in Knidos, the Aegean Sea and matched from GC/MS memory (Rt: 28.70-28.80).

![Figure 2. GC/MS chromatogram of 3-nitrophthalic acid](image-url)
Figure 3. Spectra of 3-nitrophthalic acid a) detected from mussels collected from the Çanakkale Strait; b) taken from the HP memory.

Phthalates are generally found in sea water as pollutants and reacting with NOx in the exhaust gas. In an earlier work, 3-nitrophthalic acid was for the first time found in sea water (Cumali and Guven 2007). In this study, 3-nitrophthalic acid was also found in the mussels collected from Lapseki in the Çanakkale Strait where marine traffic is very heavy due to transit tankers and ships as well as smaller boats working across the Strait all day and their exhaust is discharged into sea water.

Another nitro-aromatic compound, 3-nitrostyrene (1-ethenyl-3-nitrobenzene), was detected in the water of the Golden Horn, just under the Bridge. The GC/MS chromatogram is shown in Figures 4 and 5.

In this study, 3-nitrophthalic acid and 1-ethenyl-3-nitrobenzene (3-nitrostyrene) were found in the mussel and sea water, respectively, for the first time.

Figure 4. GC/MS chromatogram of 3-nitrostyrene
Discussion

There are many studies on the exhaust gas from vehicles. The first study from Turkey was made in 2005 by Cumali and Güven (2008). Oil pollution in mussel was investigated by Güven et al. (2009). Only the mussels in Lapseki Harbour were found contaminated by 3-nitrophthalic acid because of the heavy petroleum pollution in the area.

Human consumption of mussels collected from harbors and the areas of heavy marine traffic must be regulated by both international and national authorities.

Ege Denizi deniz suyunda ve Çanakkale Boğazı’ndan toplanan midyelerde 3-nitroftalik asit ve Haliç deniz suyunda 3-nitrostiren kirliliğinin tespiti

Özet

3-nitroftalik asit Ege Denizi, suyu örneği ile Lapseki (Çanakkale)’den toplanan midye örneklerinde saptanmıştır. 3-nitrostiren Haliç deniz suyunda saptanmıştır. 3-nitroftalik asidin midyelerde ve 3-nitrostirenin deniz suyunda saptanması literatürde ilktir.
References


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