

ORGANOCHLORINE PESTICIDES AND PAHS COMPOUNDS OCCURRENCE IN MUSSEL AND FISH LIVER FROM BLACK SEA

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Abstract

A method has been studied for the analysis of 9 POPs and 15 PAHs in mussel and fish liver from the Black Sea. The method was based on liquid-liquid extraction using n-hexane. The extracts were fractionated and cleaned up with a Florisil, respectively aluminium oxide and silica gel column. The concentrations of analytes were determined by gas chromatography with electron capture detection (GC-ECD), respectively by gas chromatography with mass spectrometer detector (GC-MS).

Keywords: POPs, PAHs, GC-ECD, GC-MS

Introduction

Many persistent, bioaccumulated POPs have been extensively used in many countries, but nowadays their use has been prohibited. Compounds such as DDT and dieldrin have become globally enriched in food chains (1-3).

PAHs are widespread environmental contaminants and represent a very important group of chemical carcinogens (4). So, these pollutants pose a threat to human beings and aquatic organisms (5).

This study aims to evaluate the occurrence of important organic contaminants, such as POPs and PAHs in biota (mussel and fish) collected from the Black Sea.

Sampling

Mussels' species samples (*Mytilus* sp.-*MandScapharca* sp.-S) were collected from two different locations on the Romanian Black Sea coast (Midia -Mid and Vama Veche -VV). Fish species samples (*Apollonia melanostomus* -AM, *Ponticola cephalargoides* -PC, *Blennius sanguinolentus* -BS) were collected from three different locations in the Black Sea (Midia -Mid, Eforie Nord- EN and Agigea -Agi). All samples were collected in 2002. The samples were wrapped in polyethylene bags and frozen at 4 °C.

A 5-10 g amount of fish and mussel liver was homogenized with anhydrous Na₂SO₄ and extracted with n-hexane in a Soxhlet device.

Extraction

The extracts were filtered and concentrated by rotary evaporator. In order to separate the PAHs, an aliquot of the extract was applied to 5 g of activated aluminium oxide and silica-gel column, respectively 5 g of activated Florisil column for POPs, topped with 1 cm of anhydrous sodium sulfate, which was pre-washed with n-hexane. The columns were eluted with n-hexane-dichloromethane (3:1). Each fraction was concentrate to 1 mL using the Kuderna – Danish concentrator. The concentrated aliquot was blown down with nitrogen, the internal standards (9,10 dihydroanthracene and trichlorobiphenyl) were added, and the final volume was injected.

Instrumental analysis

A HP 5890 gas chromatograph equipped with an electron capture detector (ECD) was used for POPs analysis. The separation was performed on a fused-silica capillary column HP-5, 30m x0.32mm x0.25µm film thickness.

PAHs analyses were performed using a HP5890 gas chromatograph interfaced to a HP5972 mass selective detector (6). The analyses were operated in SIM mode. Identification was made on the basis of matching the mass spectrum and the retention time of the compound to that of a known standard.

Results and discussion

Concentrations of POPs and PAHs measured in mussel and fish liver from Black Sea are given in Table 1 and Table 2. It can be observed that PAHs are the main contaminants in all samples. Aldrin was found at high levels, while HCB and heptachlor concentrations were low.

For fishes collected from the same location (Eforie Nord) it could be seen that AM contained higher amount of pollutants.

These analyses indicate that levels of HCB are much lower than concentrations measured in fishes from Danube Delta (7) and DDT was not detected comparatively with samples from Sea of Japan (8).

Table 1. Concentrations of PAHs and some POPs in the Black Sea biota.

| Compound (ng/g) | Site | ΣPAH | HCB | ΣDDT | Heptachlor |
|-----------------|------|--------|------|------|------------|
| M | VV | 486.09 | nd | nd | nd |
| S | Mid | 49.63 | nd | nd | nd |
| AM | EN | 37.16 | nd | nd | 102.20 |
| | Mid | 262.57 | nd | nd | 89.11 |
| BS | Agi | 0.42 | 5.88 | nd | nd |
| PC | Agi | 168.82 | 8.28 | nd | nd |
| | EN | 57.85 | nd | nd | nd |

Table 2. Concentrations of some POPs in the Black Sea biota.

| Compound | Site | Lindan | Aldrin | Dieldrin | Dieldrin |
|----------|------|--------|---------|----------|----------|
| M | VV | 430.43 | 787.52 | 286.52 | nd |
| S | Mid | nd | 660.61 | nd | nd |
| AM | EN | 65.34 | 1231.92 | 126.99 | nd |
| | Mid | nd | 287.20 | 118.49 | nd |
| BS | Agi | nd | nd | nd | nd |
| PC | Agi | nd | nd | nd | nd |
| | EN | nd | nd | nd | nd |

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