# ANALYSIS OF ORGANOCHLORINE PESTICIDES IN BLACK SEA SEDIMENTS

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**Abstract.** A study was conducted to investigate the pesticides residues in sediments collected from different Constanta harbour berths Black Sea water. Determination of these pollutants is carried out in order to evaluate the pollution potentials and hazard in Black Sea sediments. An Agilent gas chromatograph equipped with an electron capture detector (GC-μECD) was used for organochlorine pesticides (OCP's) analysis from sediments samples, after extraction and clean-up step. The OCP's total concentration (sum of 11 compounds) is generally quite low (in order of μg\kg).

**Keywords**: OCPs, sediments, GC-μECD, Black Sea

## 1. Introduction

According to the Stockholm Convention on Persistent Organic Pollutants, 9 of the 12 most dangerous and persistent organic chemicals are pesticides (UNEP/UNDP, 2001).

Owing to their high capacities for bioaccumulation and toxicities in organisms, these compounds pose threats to ecosystems and human health (Gilden et al., 2010). Pesticides have great affinity for fatty molecules what makes it easier to be accumulated in the fat tissue of organisms; as a consequence they can be biomagnify along the food chain, where its degradation products are more toxic or permanent than the original compound (Henao and Nieto, 2004). In fish, the tissue accumulation grade in males is proportional to the age (Tricklebank et al., 2002) and its trophic level (Manirakiza et al., 2002).



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Their intensive use throughout the agricultural world for crop protection in the past has led to their ubiquity in the environment (FAOUN, 2002).

Residues of OCPs continue to detect in many areas. OCPs can be introduced into the coastal environment by a variety of processes, such as discharge of domestic sewage and industrial wastewater, runoff from non-point sources, agricultural inputs, and atmospheric deposition. The marine sediment is one of the most important reservoirs of these contaminants. Because of their low water solubility, OCPs have a strong affinity for suspended particulates and subsequently settle down to sediments. Marine sediments are thought to be one of their major sinks (Voorspoels et al., 2004). Therefore, the investigation of distribution of OCPs in sediments can provide a valuable record of contamination in the aquatic environments (Doong et al, 2002).

The Black Sea is the world's largest land-locked sea and has an area of 4.2 · 105 $km^2$ with average depth of 1240 m, respectively. Ninety percent of its water mass is anoxic, thus it contains the world's largest anoxic water mass (Konovalov et al, 2006).

The aim of this study is to determine the concentration of organochlorine pesticides in sediments collected from different berths of Black Sea port of Constanta. Determination of these pollutants is carried out in order to evaluate the pollution potentials and hazard in Black Sea sediments.

## 2. Experimental

### 2.1. SAMPLING

Different sediments samples were purchased from the berths of Black Sea port of Constanta.

Constanța harbour is both a maritime and a river port. Daily, more than 200 river vessels are in the port for cargo loading or unloading or waiting to be operated. It has a handling capacity of 100,000,000 tons per year and 156 berths, of which 140 berths are operational. Is importing crude oil, diesel, gas and exporting refined products and chemical products, iron ore, bauxite, coal and coke.

Surface sediment samples were taken with a grab sampler in November of 2009. The top 1-cm layers were carefully removed with a stainless steel spoon for subsequent analysis. All the samples were packed in aluminum boxes and immediately stored at 20$^{o}$C until required.

## 2.2. REAGENTS AND SOLUTIONS

Standards of pesticides: 2,4,5,6 tertrachlor-m xilen, α-HCB, ß-HCB, Heptachlor, Endosulfan I, Dieldrin, Endrin, 4,4-DDD, 4,4-DDT, Methoxychlor, 2,10-Chlorphenyl were supplied by International Atomic Energy Agency, Monaco laboratory.

Florisil was assayed for preconcentration step as sorbent material of variable polarities. It (60 – 100 mesh) was obtained from Fluka (packed in Switzerland) and was activated overnight (12h) at 130$^{o}$C before use. Anhydrous sodium sulphate (granulated for residue analysis – Merck) was activated at 200$^{o}$C for 2h before use. As eluents two organic solvents there were used: n-hexane, supplied by Merck, Darmstadt, Germany and dichloromethane supplied by J.T. Baker.

## 2.3. EXTRACTION AND CLEAN-UP

Each sediment sample was placed into a homogenizer jar and mixed with anhydrous sodium sulphate in an amount three times greater than the weight sample. The homogenized subsamples were freeze-dried and OCPs were extracted with Soxhlet apparatus. Approximately, 8 g sediment was placed into a thimble filter. The Soxhlet extraction used takes 8 ± 0.5 h with hexane (250 ±10 mL) as solvent.

The extracts were then preconcentrated to a 15 ± 2 mL volumes on a vacuum using a rotary evaporator. The extract was further treated with activated copper powder to remove sulfur compounds. A Florisil column chromatography was used to clean-up the extracts. A home-made glass column containing a piece of glass wool on a glass frit was filled with 5 g of activated Florisil and about 1 g of anhydrous sodium sulfate was added on the top. The organochlorine pesticides were eluted with hexane: dichlormethane (3:1) mixture.

The elutes were concentrated to about 1–2 ml on a rotary evaporator and then transferred to 10 ml glass tubes with small amounts of hexane. The solvent in the glass tube was entirely evaporated under a gentle stream of nitrogen and the precipitates were redissolved in 1 ml hexane. The extracts were analyzed with an Agilent gas chromatograph (model 6890 HP) equipped with an electron capture detector (GC-μECD). The internal standard used was 2,4,5, trichlorobiphenile (10 ng/μL).

2.4. INSTRUMENTAL ANALYSIS

Gas chromatography was performed using a Agilent 6890 gas chromatograph equipped with a electron capture detector and a capillary column (HP-5 30x0.32mmx0.25µm) using helium carrier gas at a flow rate of 1.5mL/min. The oven temperature programmed was: initial temperature isothermal, at 60°C, for 1 min, then from 60 to 300°C at 20°C/min, for 10 min. Injector and detector temperatures were 250°C, respectively 300°C. The injection was carried out splitless and the injection volume was 1 µl. Quantification of the pesticides was performed by comparing the peak areas to that of a calibration curve of standards.

## 3. Results and Discussion

The residual concentrations of the organochlorine pesticides in surface sediments are summarized in Tables 1 and 2. OCP's total concentration (sum of 11 compounds) in sediments collected in the Black Sea is generally quite low (in order of µg\kg).

TABLE 1. Concentrations of organochlorine pesticides in surface sediment (µg\kg) of Constanta harbour

| analyte | berth 61 | berth 68 | berth 111 | berth 112 | berth 113 |
|---|---|---|---|---|---|
| tetrachloro-m xylene | 0.060 | 0.070 | 0.006 | 0.005 | 0.060 |
| α-HCB | 0.100 | 0.003 | 0.0003 | 0.002 | 0.020 |
| ß-HCB | 0.010 | 0.007 | 0.002 | 0.003 | 0.030 |
| Heptachlor | 0.050 | 0.009 | 0.004 | 0.002 | 0.060 |
| Endosulfan | - | 0.002 | 0.006 | 0.0004 | - |
| Dieldrin | - | 0.004 | 0.002 | 0.0002 | 0.050 |
| Endrin | 0.050 | 0.002 | 0.001 | 0.001 | 0.100 |
| p,p'-DDD | 0.180 | 0.007 | - | 0.005 | 0.200 |
| p,p'-DDT | 0.070 | 0.004 | 0.002 | 0.001 | 0.300 |
| Methoxychlor | - | 0.013 | 0.010 | 0.020 | - |
| 2,10-clorophenyl | 1.460 | 0.023 | 0.006 | 0.003 | 1.900 |

As shown in Tables 1 and 2, the total concentration of organochlorine pesticides in surface sediments revealed a wide range of fluctuation, from 0.0212 to 2.7200 µg\kg dry weight with a mean concentration of 0.5254 µg\kg.

The highest concentration was found in sediments from berth 112 (1.9 µg\kg - 2,10 chlorophenyl) while the lowest concentration (0.0002 µg\kg) was found in sediments collected from berth RR3 and berth 122 for dieldrin, respectively for α-HCB. The detected OCPs in sediments of the Black Sea are within the limits permitted by the National Environment Agency (0.01 mg\kg) (Order no. 161/2006). DDD which ranged from 0.0007 to 0.200 µg\kg dw was detected in 90% of samples. Concentrations of DDD and DDT in Black Sea sediments were comparable to those of the Baltic Sea sediments (Pikkarainen, 2007), Black Sea sediments from Rusia (Fillman et al., 2002) and lower than those encountered in Alexandria harbor, Egypt (Barakat et al., 2002). The DDT compounds in sediments may be mainly derived from DDT-treated aged and weathered agricultural sources (Bakan and Ariman, 2004).

TABLE 2. Concentrations of organochlorine pesticides in surface sediment (µg\kg) of Constanta harbour

| analyte | berth 114 | berth 122 | berth RR3 | berth RR4 | berth RR5 |
|---|---|---|---|---|---|
| tetrachloro-m xylene | 0.030 | 0,050 | 0.003 | 0.0006 | 0.004 |
| α-HCB | 0.006 | 0.005 | 0.0009 | 0.0002 | 0.0008 |
| ß-HCB | 0.001 | 0.008 | 0.002 | 0.0004 | 0.001 |
| Heptachlor | 0.010 | 0.020 | 0.001 | 0.0007 | 0.002 |
| Endosulfan | 0.0008 | 0.0004 | - | - | 0.001 |
| Dieldrin | 0.010 | 0.008 | 0.0008 | 0.0006 | 0.001 |
| Endrin | 0.004 | 0.003 | 0.0006 | 0.001 | 0.002 |
| p,p'-DDD | 0.002 | 0.0007 | 0.0009 | 0.002 | 0.002 |
| p,p'-DDT | 0.0007 | 0.002 | 0.001 | 0.004 | 0.020 |
| Methoxychlor | 0.020 | 0.003 | 0.009 | - | 0.040 |
| 2,10-clorophenyl | 0.007 | 0.004 | 0.002 | 0.020 | 0.009 |

## 4. Conclusions

Recorded values of OCPs were not especially high in comparison to levels reported from sediments of other coastal environments, but their presence indicates a significant degree of pollution and permits the identification of principal contamination sources. Based on our experimental findings, it should be concluded that the environmental actuality of Black Sea is still contaminated by some pollutants. It is also necessary to monitor their distribution in the atmosphere, sediment and marine mammals, and to evaluate their long-term harmful effects to marine organisms in the Black Sea.

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