

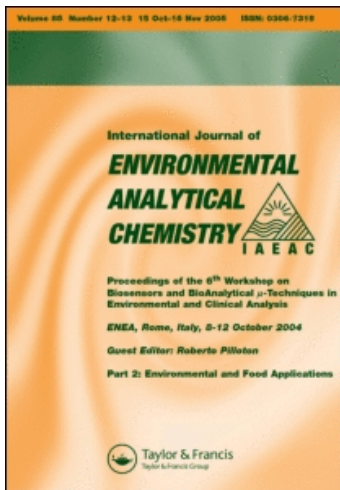
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## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Determination of organochlorine pesticide residues in water, sediment, and fish samples from the Meriç Delta, Turkey

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**To cite this Article** Erkmen, Belda and Kolankaya, Dürdane(2006) 'Determination of organochlorine pesticide residues in water, sediment, and fish samples from the Meriç Delta, Turkey', *International Journal of Environmental Analytical Chemistry*, 86: 1, 161 – 169

**To link to this Article:** DOI: 10.1080/03067310500247926

**URL:** <http://dx.doi.org/10.1080/03067310500247926>

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## Determination of organochlorine pesticide residues in water, sediment, and fish samples from the Meriç Delta, Turkey

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(Received 28 September 2004; in final form 26 March 2005)

This study had been carried out between May 2002 and August 2003 in Meriç Delta, Turkey which is located at a site where the Meriç River falls to the Aegean Sea. Residues of organochlorine pesticides (OC) in surface water, sediment, and fish (*Cyprinus carpio*) samples from Meriç Delta were analysed by gas chromatography. The results of the study showed that all analysed 20 organochlorine pesticides and their residues have been widespread throughout the study area. According to the results, it was found that the concentrations of these selected organochlorine pesticides in fish (*Cyprinus carpio*) samples were higher than in water and sediment samples. Because of the low water solubility of the organochlorine compounds, it is expected that any organochlorine pesticides present in the study area, will be preferably adsorbed to sediment or bioaccumulated in fish. The  $\alpha$ - and  $\beta$ -HCH were the predominant HCH isomers in all analysed fish samples and ranged between 319.5 and 968.15 ng g<sup>-1</sup> and between 397.5 and 876.4 ng g<sup>-1</sup>, respectively. The concentration levels of p,p'-DDT (ranging from 2.68 to 52.45 ng g<sup>-1</sup>) in all analysed fish samples were consistently higher than its metabolite p,p'-DDE, indicating a recent use of this organochlorine pesticide in the area. We have analysed the distribution characteristics of individual organochlorine pesticide and found that  $\alpha$ -,  $\beta$ -HCH, p,p'-DDT, p,p'-DDE,  $\beta$ -endosulphan, heptachlore epoxide, and endrin ketone were the most common organochlorine pesticides contaminants in the study area.

**Keywords:** Meriç Delta; Organochlorine pesticides; Residue; Biota

### 1. Introduction

Meriç Delta is located at a site where the Meriç River falls to the Aegean Sea. The Meriç Delta is rich in terms of biological resources and is an internationally important wetland because of its location along a bird-migration route. In this region, the most important economic activities are fisheries and agricultural activities. Over the last decades, the aquatic ecosystems in the region have been contaminated by persistent pollutants of agricultural and industrial origin. Industrial waste products from Turkey and neighbouring countries intensively pollute the Meriç River. The Ergene River, which is one of the main tributaries of the Meriç River, is heavily loaded with the unrefined wastes of hundreds of industries. Moreover, domestic wastes and the

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pollutants from the agricultural areas, especially the rice fields, contribute considerably to the pollution.

Environmental contamination of natural waters by pesticide residues is of great concern. The increased use of various types of pesticides, particularly organochlorine pesticides, has led to concern regarding the potential for contamination of environmental media (i.e. water, sediment, and biota) and associated effects on human health and wildlife [1]. The use of synthetic organic compounds, such as organochlorine insecticides, was widespread in the world between the 1940s and the 1980s. Being persistent, traces of organochlorine compounds could be the result of either recent use or long duration [2].

Input pathways of organochlorine pesticides into river environments include discharge of domestic sewage and industrial wastewater, run-off from nonpoint sources, and direct dumping of wastes into the river. Synthetic organochlorines such as DDTs, chlordanes, and cyclodienes are highly resistant to degradation by biological, photochemical, or chemical means. They are also liable to bioaccumulate and are toxic and probably hazardous to humans and/or environmental health [3]. Their use has been prohibited in Turkey as well as in other countries, after evidence of their toxicity, persistence, and bioaccumulation in the environment became available.

The main objective of this study was to identify and quantify organochlorine residues in water, sediments, and fish samples so as to assess the extent of contamination of Meriç Delta by the organochlorine pesticides and evaluate the toxicological significance of the findings.

## 2. Experimental

Location of sampling sites in the study area is shown in figure 1. Eight stations were selected. All samples were collected from May 2002 to August 2003.

After a preliminary study, eight stations were selected in Meriç Delta, Turkey to determine organochlorine pesticide residues in water and sediment samples, whereas five stations were selected for the fish samples. Water and sediment samples were collected in November and August 2002 and March and June 2003 from the stations (1, 2, 3, 4, 5, 6, 7, 8) indicated in figure 1. These samples were collected 0.5 m below the water surface in 1 L precleaned glass bottles and kept at +4°C. The upper 10 cm of sediments was collected with an Ekman sampler in sterile 250 mL glass bottles. Twenty *Cyprinus carpio* fish were collected from each of five stations (1, 3, 4, 5, 7). As much as possible, similar-sized fish samples were collected from selected stations. Each fish was measured (cm), tagged and placed on ice and later frozen until analysis. Water, sediment, and fish samples were taken to a laboratory in Ankara.

Organochlorine extraction of water samples was carried out according to the Zweig method [4]. In this method, a 500 mL water sample was extracted with 25 mL of *n*-hexane into a 1 L reparatory funnel three times. The combined extracts were dried over anhydrous sodium sulphate (0.5 g). The extracts were evaporated at 50°C to 1–2 mL for the determination of water samples. Sediment samples were extracted with *n*-hexane using Soxhlet apparatus for 8 h [5]. The extract was cleaned on a partially deactivated Fluorisil column.

At the laboratory, the muscle tissue from each fish was homogenized separately in a high-speed blender until a paste-like consistency was formed. After preparing the

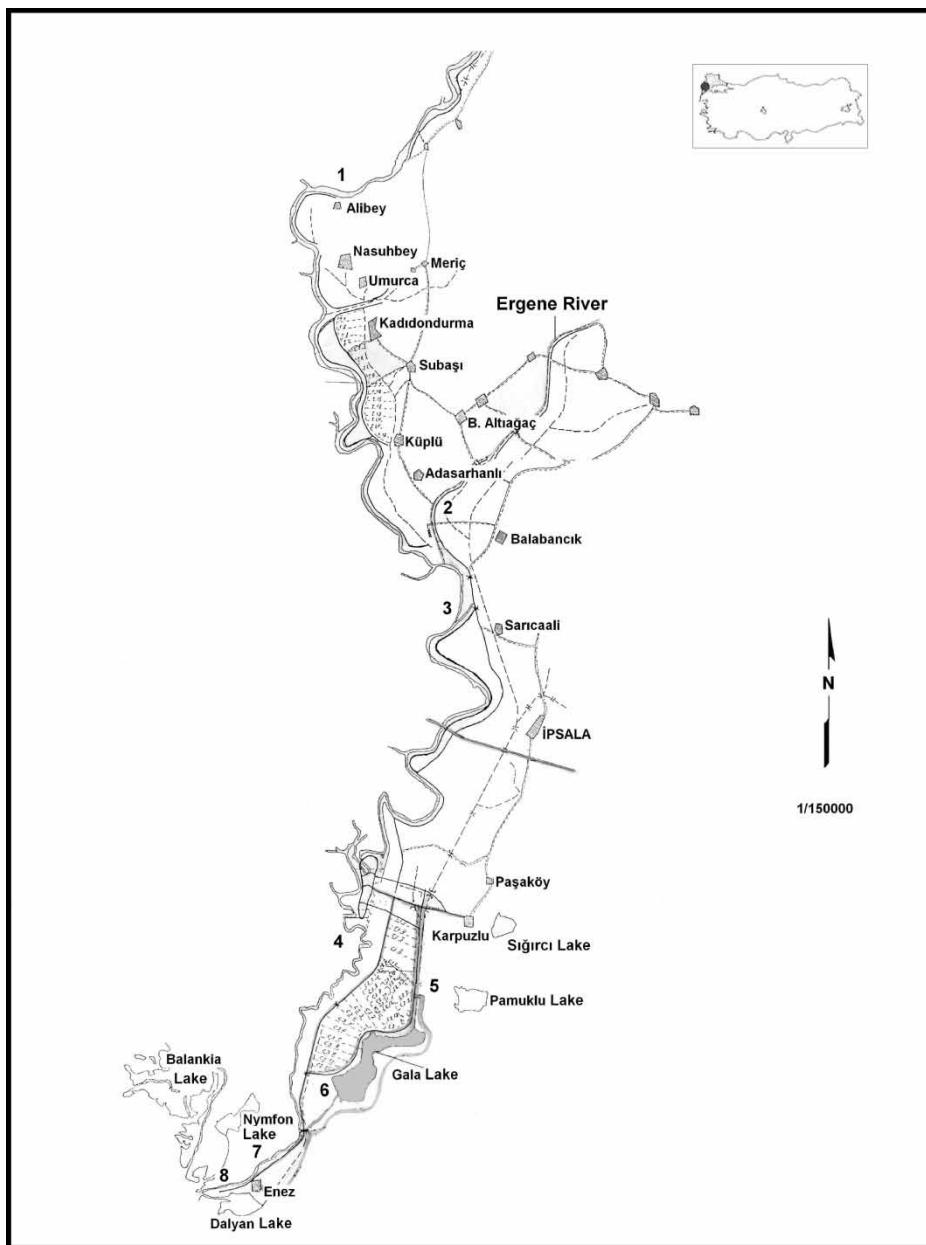


Figure 1. Location of sampling sites in the study area.

homogenate, 20 g of the sample was taken and mixed with 20 g of anhydrous sodium sulphate. This mixture was then ground in a mortar until it achieved the consistency of a free-flowing powder. The powder was transferred to a paper thimble and extracted in a Soxhlet apparatus using 250 mL of solvent (*n*-hexane:dichloromethane, 1:1) for 6 h at 45°C. The extract was then evaporated to dryness to calculate the fat content. Then, 0.1 g of fat was taken and cleaned up through glass chromatography column

with deactivated Florisil (mesh: 60–100  $\mu\text{m}$ ), and the extract was eluted through a glass column with 100 mL of eluting mixture (*n*-hexane : dichloromethane, 1 : 1). The extract was then evaporated to dryness and made final volume (5 mL) with *n*-hexane for gas-chromatographic analysis [1]. Gas-chromatography analysis was carried out on a Chrompack-SFC Instrument 138 A with a Ni electron capture detector (ECD), automatic sampler, digital processor, and 4% SE-30/6% QF-column at 270°C. Nitrogen was used as a carrier gas at a flow rate of 40  $\text{m min}^{-1}$ .

Results are presented as minimum, maximum, and geometric means. According to this method, the detection limit is 0.0001  $\text{ng g}^{-1}$ . Means were the concentration of the non-detected analytes treated as zero. Values below detection limits were assigned as a non-detectable (nd).

### 3. Results and discussion

In Turkey, the use of organochlorine pesticides was controlled in the late 1970s, but effective restrictions were not imposed until the 1980s. Between 1976 and 1983, the annual use of organochlorine insecticides in Turkey was 1000–2000 tonnes [3]. Despite this restriction, pesticide residues have been found in fresh water, sediment, and biota [6,7], indicating that pesticides stored in sediments will continue to be biologically available due to their long residence time. Although the use of organochlorine compounds such as DDT is not allowed, the presence of such compounds in rivers, streams, lake, and domestic and industrial discharges also indicate their illegal use, particularly in agriculture.

In this study, analyses were carried out on samples from different localities and organisms in Meriç Delta. Tables 1–3 illustrate the concentrations of organochlorine pesticide residues in water, surface sediments and fish samples from Meriç Delta. The results of the study showed that analysed 20 organochlorine pesticides and their residues were detected in selected stations from the study area. In these tables, organochlorine pesticide residues in fish samples were generally higher than residue levels in water and sediment samples. Because of the low water solubility of the organochlorine compounds, it is expected that any organochlorine pesticides present in the study area will be preferably adsorbed to sediment or bioaccumulated in fish. Indeed, the levels of these compounds were the lowest in water samples, and the levels of organochlorine compounds were considerably higher in sediment and fish samples.

The analysed water samples showed the presence of the following organochlorine pesticide residues at concentrations above the limits of the method of detection. Concentrations of OC pesticides ranged from 0.466 to 1.127  $\mu\text{g L}^{-1}$  for  $\Sigma$ -HCHs, not detected (nd) to 0.527  $\mu\text{g L}^{-1}$  for  $\Sigma$ -heptachlor, nd to 0.04  $\mu\text{g L}^{-1}$  for aldrin, nd to 0.2  $\mu\text{g L}^{-1}$  for  $\Sigma$ -chlordane, 0.091 to 1.66  $\mu\text{g L}^{-1}$  for  $\Sigma$ -endosulphan, nd to 1.01  $\mu\text{g L}^{-1}$  for  $\Sigma$ -DDT, nd to 0.01  $\mu\text{g L}^{-1}$  for dieldrin, and 0.047 to 0.617  $\mu\text{g L}^{-1}$  for  $\Sigma$ -endrin. In water samples, endrin aldehyde, and methoxychlor residues were not found in any station (table 1).

Among the analysed organochlorine residues, levels of sediment samples are reported in table 2. Concentrations of OCPs ranged from 0.406 to 3.243  $\text{ng g}^{-1}$  for  $\Sigma$ -HCH, 0.113 to 2.033  $\text{ng g}^{-1}$  for  $\Sigma$ -heptachlor, nd to 1.473  $\text{ng g}^{-1}$  for aldrin, nd to 1.103  $\text{ng g}^{-1}$  for  $\Sigma$ -chlordane, 0.87 to 2.667  $\text{ng g}^{-1}$  for  $\Sigma$ -endosulphan,

Table 1. Concentrations of organochlorine compounds in water ( $\text{ng g}^{-1}$  dw) at sample stations from Meriç Delta.<sup>a</sup>

	Station 1 <i>n</i> : 4	Station 2 <i>n</i> : 4	Station 3 <i>n</i> : 4	Station 4 <i>n</i> : 4	Station 5 <i>n</i> : 4	Station 6 <i>n</i> : 4	Station 7 <i>n</i> : 4	Station 8 <i>n</i> : 4
$\alpha$ -HCH	0.007 (nd–0.02)	0.033 (nd–0.1)	0.05 (nd–0.15)	0.04 (nd–0.12)	0.217 (nd–0.39)	0.147 (nd–0.32)	0.027 (nd–0.08)	0.03 (nd–0.09)
$\beta$ -HCH	0.47 (nd–0.14)	0.367 (nd–1.1)	0.41 (nd–1.23)	0.563 (nd–1.13)	0.743 (0.64–0.86)	0.683 (0.35–0.98)	1.1 (0.4–1.97)	0.457 (0.34–0.57)
$\gamma$ -HCH	nd	0.097 (nd–0.2)	nd	nd	nd	nd	nd	nd
$\Delta$ -HCH	nd	nd	0.063 (nd–0.19)	nd	nd	nd	nd	nd
$\Sigma$ -HCH	0.477	0.497	0.466	0.603	0.960	0.830	1.127	0.487
p,p'-DDE	nd	nd	nd	nd	0.107 (nd–0.22)	0.067 (nd–0.13)	nd	nd
p,p'-DDD	nd	0.26 (nd–0.47)	0.313 (0.14–0.43)	0.22 (0.1–0.29)	0.590 (0.3–0.84)	0.473 (0.12–0.75)	0.14 (0.06–0.22)	0.14 (nd–0.31)
p,p'-DDT	nd	0.267 (0.18–0.39)	0.363 (0.1–0.52)	0.18 (0.07–0.27)	0.313 (nd–0.84)	0.27 (nd–0.67)	0.28 (nd–0.71)	0.168 (nd–0.45)
$\Sigma$ -DDT	nd	0.527	0.676	0.40	1.01	0.81	0.420	0.308
$\alpha$ -Endosulphan	0.021 (nd–0.05)	0.08 (nd–0.24)	0.057 (nd–0.17)	0.043 (nd–0.13)	0.14 (nd–0.27)	0.083 (nd–0.16)	0.127 (nd–0.28)	0.07 (nd–0.17)
$\beta$ -Endosulphan	0.03 (nd–0.09)	0.597 (0.42–0.84)	0.227 (0.16–0.33)	0.38 (0.16–0.48)	0.673 (0.42–0.87)	0.61 (0.37–0.87)	0.317 (0.18–0.42)	0.103 (0.07–0.13)
Endosulphan sulphate	0.04 (nd–0.07)	0.397 (0.23–0.64)	0.16 (nd–0.36)	0.193 (0.14–0.25)	0.847 (0.61–1.01)	0.727 (0.28–1.06)	0.223 (0.15–0.28)	0.333 (0.07–0.49)
$\Sigma$ -Endosulphan	0.091	1.074	0.444	0.616	1.660	1.420	0.667	0.506
Heptachlor	0.023 (nd–0.07)	0.077 (nd–0.23)	0.06 (nd–0.18)	0.037 (nd–0.11)	0.133 (nd–0.23)	0.187 (nd–0.56)	0.2 (nd–0.56)	nd
Heptachlorepoxyde	nd	0.36 (nd–1.08)	0.467 (nd–1.4)	0.30 (nd–0.9)	0.183 (nd–0.39)	0.113 (nd–0.23)	0.233 (nd–0.7)	nd
$\Sigma$ -Heptachlor	0.023	0.077	0.527	0.337	0.316	0.300	0.433	nd
<i>cis</i> -Chlordane	nd	0.16 (nd–0.48)	0.06 (nd–0.18)	0.127 (nd–0.38)	nd	nd	nd	nd
<i>trans</i> -Chlordane	nd	0.04 (nd–0.12)	0.07 (nd–0.21)	nd	nd	nd	nd	nd
$\Sigma$ -Chlordane	nd	0.200	0.13	0.127	nd	nd	nd	nd
Endrin	nd	nd	nd	nd	nd	nd	nd	nd
Endrin aldehyde	nd	nd	nd	nd	nd	nd	nd	nd
Endrin ketone	0.427 (nd–0.58)	0.047 (nd–0.1)	0.19 (0.09–0.38)	0.097 (nd–0.21)	0.617 (0.3–0.82)	0.413 (0.24–0.59)	0.093 (nd–0.18)	0.12 (nd–0.21)
$\Sigma$ -Endrin	0.427	0.047	0.19	0.097	0.617	0.413	0.093	0.12
Aldrin	0.013 (nd–0.04)	0.028 (nd–0.085)	0.026 (nd–0.03)	0.012 (nd–0.015)	nd	nd	0.04 (nd–0.12)	nd
Dieldrin	0.01 (nd–0.03)	nd	nd	nd	nd	nd	nd	nd
Methoxychlor	nd	nd	nd	nd	nd	nd	nd	nd
$\Sigma$ -OCPs	1.041	2.450	2.925	2.192	4.563	3.773	2.780	1.421

<sup>a</sup>nd: not detectable. *n*: number of samples.

Table 2. Concentrations of organochlorine compounds in sediments (ng g<sup>-1</sup> dw) at sample stations from Meriç Delta.<sup>a</sup>

	Station 1 <i>n</i> : 4	Station 2 <i>n</i> : 4	Station 3 <i>n</i> : 4	Station 4 <i>n</i> : 4	Station 5 <i>n</i> : 4	Station 6 <i>n</i> : 4	Station 7 <i>n</i> : 4	Station 8 <i>n</i> : 4
$\alpha$ -HCH	0.313 (nd–0.94)	0.297 (nd–0.89)	0.213 (nd–0.64)	0.723 (nd–1.3)	0.77 (nd–1.67)	0.38 (nd–0.9)	0.703 (nd–1.6)	0.29 (nd–0.52)
$\beta$ -HCH	0.093 (nd–0.28)	1.513 (nd–2.29)	1.380 (nd–2.54)	0.967 (nd–1.779)	0.823 (nd–1.58)	0.757 (nd–1.25)	0.837 (nd–1.54)	0.423(nd–0.88)
$\gamma$ -HCH	nd	0.123 (nd–0.37)	0.043 (nd–0.130)	nd	0.673 (nd–1.04)	0.650	0.133 (nd–0.4)	nd
$\Delta$ -HCH	nd	1.31 (0.99–1.7)	1.093 (0.83–1.33)	1.063 (0.9–1.16)	0.437 (nd–1.08)	0.62 (nd–1.29)	1.487 (1.18–1.73)	0.36 (0.16–0.65)
$\Sigma$ -HCH	0.406	3.243	2.679	2.753	2.703	2.407	3.16	1.073
p,p'-DDE	0.337 (nd–0.82)	0.833 (0.6–1.2)	0.87 (0.38–1.2)	1.203 (0.72–1.61)	0.690 (0.45–0.9)	0.643 (0.51–0.85)	0.647 (0.56–0.7)	0.527 (0.43–0.67)
p,p'-DDD	nd	0.29 (nd–0.73)	0.77 (0.65–0.88)	1.523 (0.94–1.93)	1.317 (1.15–1.57)	1.053 (0.78–1.26)	0.857 (0.53–1.14)	0.343 (0.22–0.45)
p,p'-DDT	0.187 (nd–0.56)	0.663 (nd–1.55)	0.547 (0.1–0.83)	1.310 (1.21–1.49)	0.187 (nd–0.41)	0.217 (nd–0.39)	1.333 (0.8–1.74)	1.18 (1.1–1.29)
$\Sigma$ -DDT	0.524	1.786	2.187	1.413	2.194	0.643	2.837	2.05
$\alpha$ -Endosulphan	0.353 (0.12–0.5)	1.087 (0.11–1.52)	0.657 (nd–1.07)	1.11 (0.42–1.49)	0.24 (nd–0.72)	nd	0.343 (0.12–0.73)	0.37 (0.12–0.78)
$\beta$ -Endosulphan	0.377 (nd–0.64)	1.313 (0.9–1.97)	0.557 (0.24–0.8)	0.62 (0.1–1.08)	1.1 (0.63–1.62)	0.797 (0.38–1.06)	1.01 (0.78–1.25)	0.633 (0.14–0.92)
Endosulphan sulphate	0.14 (nd–0.24)	0.267 (nd–0.8)	0.32 (nd–0.73)	0.603 (0.26–0.85)	0.21 (nd–0.37)	0.15 (nd–0.3)	0.18 (0.12–0.23)	1.193 (0.97–1.47)
$\Sigma$ -Endosulphan	0.87	2.667	1.447	2.447	1.55	0.947	1.533	2.196
Heptachlor	0.293 (0.1–0.41)	0.32 (nd–0.73)	nd	0.59 (nd–1.1)	0.273 (nd–0.82)	nd	0.24 (nd–0.4)	nd
Heptachlorepoxyde	0.493 (nd–0.79)	1.14 (nd–2.32)	1.033 (nd–1.7)	1.443 (1.3–1.62)	0.157 (nd–0.47)	0.113 (nd–0.34)	0.513 (nd–1.28)	0.34 (nd–0.91)
$\Sigma$ -Heptachlor	0.786	1.460	1.033	2.033	0.43	0.113	0.753	0.34
<i>cis</i> -Chlordane	nd	0.3 (nd–0.9)	0.327 (nd–0.98)	0.29 (nd–0.87)	0.093 (nd–0.28)	0.063 (nd–0.19)	nd	nd
<i>trans</i> -Chlordane	nd	0.337 (nd–1.01)	0.403 (nd–0.78)	0.813 (nd–1.23)	nd	nd	0.643 (nd–1.04)	0.44 (nd–0.8)
$\Sigma$ -Chlordane	nd	0.637	0.730	1.103	0.093	0.063	0.643	0.44
Endrin	0.3 (nd–0.9)	0.28 (nd–0.84)	0.597 (nd–1.34)	0.27 (nd–0.81)	0.437 (0.33–0.52)	0.35 (0.21–0.45)	0.260 (nd–0.78)	0.23 (nd–0.69)
Endrin aldehyde	nd	nd	nd	nd	nd	nd	nd	nd
Endrin ketone	0.297 (0.09–0.68)	1.16 (0.48–1.9)	0.44 (0.16–0.7)	1.857 (1.8–1.92)	1.15 (0.93–1.3)	0.897 (0.75–1.02)	1.210 (1.08–1.45)	0.99 (0.84–1.13)
$\Sigma$ -Endrin	0.597	1.44	1.037	2.127	1.587	1.247	1.470	1.220
Aldrin	0.58 (0.24–0.9)	nd	1.473 (1.2–1.73)	0.57 (0.26–0.79)	nd	nd	0.597 (0.21–0.9)	0.207 (0.15–0.27)
Dieldrin	0.007 (nd–0.02)	0.25 (nd–0.75)	0.65 (0.55–0.77)	0.153 (nd–0.46)	nd	nd	0.223 (nd–0.67)	0.083 (nd–0.25)
Methoxychlor	nd	nd	nd	nd	nd	nd	nd	nd
$\Sigma$ -OCPs	3.770	11.483	11.236	12.599	8.474	5.420	11.216	7.609

<sup>a</sup>nd: not detectable. *n*: number of samples.

Table 3. Concentrations of organochlorane compounds in fish (*Cyprinus carpio*) (ng g<sup>-1</sup> fat) at sample stations from Meriç Delta.<sup>a</sup>

	Station 1 <i>n</i> = 13	Station 3 <i>n</i> = 12	Station 4 <i>n</i> = 12	Station 5 <i>n</i> = 16	Station 7 <i>n</i> = 11
α-HCH	545.48 (nd–1909)	319.5 (175–1377)	957.75 (nd–1829)	327.58 (nd–984)	968.15 (124–2089)
β-HCH	413.7 (174–1263)	876.4 (177–5640)	510.58 (nd–1953)	397.5 (105.7–376)	485.13 (149–918.5)
γ-HCH	0.86 (nd–2.24)	2.49 (2.5–17.5)	1.73 (nd–7.3)	0.49 (nd–4.2)	1.68 (nd–3.9)
Δ-HCH	2.81 (nd–16)	nd	nd	nd	1.93 (nd–7.6)
Σ-HCH	962.85	1198.39	1470.06	725.57	1456.89
p,p'-DDE	2.2 (nd–8.1)	14.03 (nd–62.6)	6.65 (nd–33.3)	4 (nd–45.5)	9.8 (nd–35.1)
p,p'-DDD	1.26 (nd–7.19)	8.83 (nd–63.1)	nd	4.44 (nd–71)	nd
p,p'-DDT	2.68 (nd–10.04)	31.04 (6.5–104)	41.075 (nd–98)	46.94 (nd–132.2)	52.45 (nd–88)
Σ-DDT	6.140	54.26	47.73	55.380	62.25
α-Endosulphan	1.13 (nd–8)	8.31 (8.3–61)	1.05 (nd–12.6)	nd	3.8 (nd–16)
β-Endosulphan	22.98 (nd–22.98)	20.0 (nd–44.3)	59.87 (nd–72.6)	19.69 (nd–72.4)	43.46 (nd–86.8)
Endosulphan sulphate	4.23 (nd–51.5)	7.63 (nd–59.2)	25.1 (nd–81.1)	40.4 (nd–448)	35.58 (nd–99)
Σ-Endosulphan	28.340	35.94	86.02	60.09	82.84
Heptachlor	4.15 (nd–32.1)	nd	1.873 (nd–12.9)	1.18 (nd–5.9)	1.81 (nd–5.2)
Heptachlorepoxyde	1.25 (nd–4.1)	3.041 (nd–15.4)	1.62 (nd–11.2)	1.92 (nd–14.5)	2.44 (nd–8.5)
Σ-Heptachlor	5.4	3.04	3.50	3.1	4.25
cis-Chlordane	nd	nd	11.68 (nd–130.6)	42.48 (nd–285)	8.05 (nd–46.6)
trans-Chlordane	1.85 (nd–17.7)	3.5 (nd–18.8)	2.22 (nd–2.22)	1.33 (nd–7.1)	2.1 (nd–16.1)
Σ-Chlordane	1.85	3.50	13.9	43.81	10.15
Endrin	8.06 (nd–73.3)	15.0 (nd–54.9)	30.0 (nd–82.9)	31.5 (nd–82.7)	30.72 (nd–70.6)
Endrin aldyde	4.4 (nd–34.7)	4.016 (3–25.2)	11.73 (nd–42.6)	1.91 (nd–17.4)	13.1 (nd–53.2)
Endrin ketone	17.04 (nd–92.9)	nd	85.25 (nd–392)	63.62 (nd–585)	49.92 (nd–171.2)
Σ-Endrin	29.50	91.42	126.98	97.03	93.74
Aldrin	nd	nd	nd	nd	nd
Dieldrin	1.35 (nd–6.16)	8.78 (nd–54.3)	9.6 (nd–30.2)	8.6 (nd–40.6)	17.78 (nd–65.3)
Methoxychlor	5.79 (nd–18.26)	50.93 (nd–152.7)	40.62 (nd–176.6)	41.38 (nd–122)	30.6 (nd–87.1)
Σ-OCPs	1041.22	1446.26	1798.41	1034.96	1758.85

<sup>a</sup>nd: not detectable. *n*: number of samples.



0.524 to 2.837 ng g<sup>-1</sup> for  $\Sigma$ -DDT, nd to 0.650 ng g<sup>-1</sup> for dieldrin, and 0.597 to 2.127 ng g<sup>-1</sup> for  $\Sigma$ -endrin. Methoxychlor residues were not found in any station.

Among the analysed organochlorine residues, levels of fish samples are reported in table 3. Concentrations of OC pesticides in fish samples ranged from 725.57 to 1470.06 ng g<sup>-1</sup> for  $\Sigma$ -HCH, 3.04 to 5.4 ng g<sup>-1</sup> for  $\Sigma$ -heptachlor, 1.85 to 43.81 ng g<sup>-1</sup> for  $\Sigma$ -chlordane, 28.34 to 86.02 ng g<sup>-1</sup> for  $\Sigma$ -endosulphan, 6.14 to 62.25 ng g<sup>-1</sup> for  $\Sigma$ -DDT, 1.35 to 17.78 ng g<sup>-1</sup> for dieldrin, 29.5 to 126.98 ng g<sup>-1</sup> for  $\Sigma$ -endrin, and 5.79 to 50.93 ng g<sup>-1</sup> for methoxychlor.

We have analysed the distribution characteristics of individual organochlorine pesticide components and found that  $\alpha$ -,  $\beta$ -HCH, p,p'-DDE, p,p'-DDT,  $\beta$ -endosulphan, heptachlor epoxide, and endrin ketone were the most common organochlorine pesticides contaminants. Similar results for OC pesticide levels in aquatic ecosystems and organisms have been documented in recent investigations [2, 8–11].

In most of the sediments of the stations from Meriç Delta, p,p'-DDE appeared to be the dominant DDT metabolite, which is reasonable given that DDE is able to bind more strongly to soil than DDT [9]. These results indicated that historical DDT input was probably the most important source of DDTs. But in water and fish samples, the situation was not the same, showing a different distribution with the highest concentration for DDT and lowest concentration for DDE. Some researchers have concluded that DDT, aldrin, and heptachlor have been found in higher quantities than their converted products [7], although the usual route of metabolism of DDT by insects appears to be through DDE. The reason is most probably its illegal applications of DDT in this region.

Considering the groups of HCHs (HCHs =  $\alpha$ -HCH +  $\beta$ -HCH +  $\gamma$ -HCH +  $\lambda$ -HCH), the predominance of  $\alpha$ - and  $\beta$ -HCH in all water, sediment, and fish samples was clearly observed. High HCH concentrations in analysed samples indicate the usage of HCH as a pesticide in this region. Because the  $\beta$ -HCH isomer is the most persistent with respect to microbial degradation and has the lowest volatility, detection of  $\beta$ -HCH in soils, sediments, and water is probably indicative of local technical HCH contaminants [12].

The  $\alpha$ - and  $\beta$ -HCH isomers were the predominant HCH isomers in all fish samples and ranged between 319.5 ng g<sup>-1</sup> of fat for station 3 and 968.15 ng g<sup>-1</sup> of fat for station 7 and 397.5 ng g<sup>-1</sup> of fat for station 5 and 876.4 ng g<sup>-1</sup> of fat for station 3, respectively. It is evident that the proportions of HCH isomers in the fish samples reflect the technical mixture composition (approximately 65%  $\alpha$ ; 10%  $\beta$ ; 15%  $\gamma$ -HCH and 10% other isomers). Considering also the persistence order of these isomers ( $\alpha < \gamma < \beta$ ) [13], these results indicated that historical HCH input and a relatively recent use of HCH in the study area can be suggested as possible explanations.

In this study, it was established that aldrin had a higher concentration than its epoxide analogue dieldrin in sediment samples in all stations. Normally, aldrin is converted to its epoxide analogue by mammals, soil micro-organisms, plants, and insects [14]. These results may be mainly due to the continuing use of OC pesticides and other environmental factors such as soil types, pH, and temperature in the study area. Aldrin was not found in any of the fish samples. In addition to these results in water, sediment, and fish samples, it was established that heptachlor epoxide was generally greater than heptachlor. This is normal, because heptachlor is metabolized to heptachlor epoxide [14].

The results of this study show that Meriç Delta is contaminated with low levels of organochlorine pesticides and their residues, but it is known that low levels of OC pesticides can cause an increase in mixed function oxidase activity in birds and fish [15].

The results demonstrate that the emission of the River Ergene represents an important point source of OC pesticides to the River Meriç. The study area receives many pollutant inputs such as discharge of effluent from factories and industrial wastes. Moreover, the presence of organochlorine pesticides in water, sediments, and fish also attributed to intense agricultural activity in the area of Meriç Delta. In addition to these factors, possible transfer of organochlorine pesticides from activities in the neighbouring countries could elevate the organochlorine pesticide contamination in the area. However, the levels of these chemicals in the fish species are expected to decline with time, since Turkey is phasing out the use of organochlorine pesticides.

### Acknowledgements

The present study was supported by the Scientific and Technical Research Council of Turkey, which is highly appreciated. The authors thank Celal Ferdi Gökçay of the Environment Engineering Lab., Middle East Technical University (METU) – Ankara, for analytical detection of OCs concentrations.

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