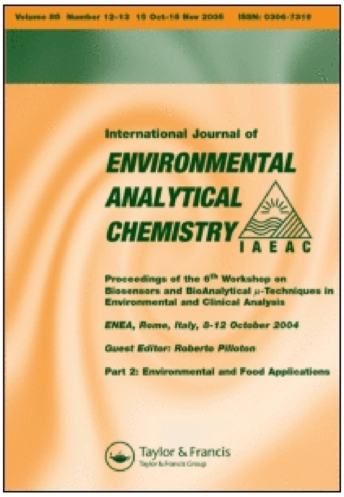

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Organochlorine pesticide reidues and their toxic effects on the environment and organisms in Turkey

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Organochlorine pesticide residues and their toxic effects on the environment and organisms in Turkey

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Persistent toxic substances (PTSs) appear in most urbanized coastal areas of the world, accumulating in water, sediments, and biota, where they cannot be eliminated efficiently, and their derivatives can be highly toxic. Like many other countries, Turkey is also facing problems concerning pesticides and other PTS residues. BHC and alpha, beta, gamma and delta isomers of HCH were determined in 16 samples of surface and ground waters and mussels in the Middle Black Sea Region, and the concentrations of PCB and organochlorine (OC) pesticide residues were analysed in the eastern Aegean Sea water and fish samples. PCBs were not detected in *Mullus barbatus* living in the Aegean Sea, and its derivatives were detected in low levels. Thirteen OC pesticides were determined in water, sediment, fish, and water birds in the Göksu Delta. Thirteen OC pesticides were analysed in the Sarıyar Dam Lake, in Sakarya basin, five lakes in Central Anatolia, and the Meriç Delta in water sediment and fish samples. Some of these pesticides were found in more or less all of the samples. Micro-organisms in soil and some saprophyte fungi detoxify chlorinated hydrocarbons by dechlorinating them. The toxicity of degraded metabolites of these insecticides, for which the Cl amounts have been reduced, decreased consequently, and toxic effects also reduced in mice when Cl was removed. Mixed cultures of micro-organisms isolated from agricultural soils were used to degrade endosulphan, carbaryl, and malathion. This result indicates that these chemicals break down in soil, resulting in a significant decrease in its toxic effects. Toxic substances cause acute, sub-chronic, and chronic effects in the environment on biota. The hermit ibises, an endemic migratory bird species, no longer visit the Birecik district. In Turkey, the reason for this is also thought to be the usage of organochlorine pesticide sprays in agricultural areas of the district. In recent years, studies have been conducted on the activation of PTSs and Cyt P450 mono-oxygenase enzymes in indicator fish species. One of these studies has been conducted on the bottom-feeding fish that live in Izmir Bay. The outcomes showed a significant decrease in the EROD activity in fish (mullet and the benthic fish common sole are used as biomonitors for PAHs and PCB-type pollutants) that have been harvested from six different stations along the Bay from the city borders towards the inner parts of the Aegean Sea. The effects of OCPs have been determined by other studies in Sarıyar Dam Lake and Meriç Delta. An increase in the EROD activity has been determined in fish living in these environments.

Keywords: Organochlorine pesticide; Residues; Water; Sediment; Biota; Toxicity; Turkey

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1. Introduction

1.1. *General situation in the country*

Pesticide usage in Turkey started with the use of DDT against all kinds of pests in the 1960s. Turkey is a land of agriculture, so agricultural pest control is essential, and the most effective method for agricultural pest control is to use chemicals. A considerable number of synthetic organochlorine pesticides have been produced and offered for usage against pests since the 1940s. Among these, aldrin, DDT, and heptachlor were used until the 1980s, when their usage was prohibited. In other countries like Turkey, especially after 1980, items primarily consumed by humans, including fish, mussels, and milk, have been analysed for organochlorine insecticide residues, and the results for the 1980s have been published or reported.

The usage of all pesticides given above started to decline after 1978, when their usage was restricted. However, they are still being used illegally in some parts of Turkey, albeit in very small amounts (tables 1 and 2). The use of 11 organochlorine and

Table 1. Pesticide usage amounts for different years.

Pesticides used	1976 (tonnes)	1977 (tonnes)	1978 (tonnes)
DDT (powder)	1889.70	538.35	553.80
DDT + BHC (powder)	689.40	714.60	638.40
Heptachlor (WP)	31.60	172.95	290.80
BHC (powder)	87.50	97.10	81.80
Lindane (WP)	96.60	70.25	21.00
40% Aldrin (WP)	9.40	9.52	7.30
Chlordane (EM)	–	7.20	36.10

Table 2. Pesticides prohibited in Turkey and their prohibition dates.

No.	Name	POP	Prohibition date
1	Dieldrin	POP	1971
2	Aldrin	POP	1979
3	Endrin	POP	1979
4	Lindane	POP	1979
5	Heptachlor	POP	1979
6	Chlordane	POP	1979
7	E-Parathion		1979
8	2,4,5-T		1979
9	Leptephos		1979
10	Clordimeform	POP	1979
11	Methylmercury		1982
12	Arsenic compounds		1982
13	Chlorbenzilate	POP	1982
14	DDT	POP	1978–1985
15	BHC		1978–1985
16	Florodifen		1987
17	Chlorpropylate		1987
18	Dinoseb		1988
19	Daminozide		1989
20	Toxaphane		1989
21	Zineb		1991
22	Azinphos ethyl		1996

Table 3. Total pesticide importation and production rates (in tonnes) in Turkey.

	1985–1990	1990–1995	1995–2000	2000–2005
Production	11.700	26.500	28.000	31.000
Importation	5.840	5.440	7.700	10.000

Table 4. Amount (tonnes) of exported pesticides in Turkey for different years.

Groups	1995	1996	1997	1998	1999
Insecticide	1565	995	832	889	1070
Acaricide	436	191	11	6	0
Oils	42	42	1	11	22
Fumigants and nematocides	14	14	26	12	8
Fungicides	212	605	366	430	551
Herbicides	691	670	411	150	23
Others	268	108	0.3	32	2
Total	3228	2625	1647.3	1530	1676

organic mercury-containing pesticides, including aldrin, endrin, DDT, dieldrin, BHC, heptachlor, chlordane, lindane, and toxophene, was prohibited in Turkey between 1971 and 1989. However, they are still being imported illegally and are sold in markets.

The number of authorized pesticides in Turkey has increased at a rate of 103%, reaching 1378 during the 8-year period until 1995, although the number was only 67 in 1986. Among these, the number of organochlorine pesticides that contain endosulphan as the active ingredient is about 55. The total pesticide production and importation rates for different years in Turkey are listed in table 3 [1, 2].

The total amounts of pesticides that are used in agricultural pest control in Turkey are as follows: 23,425 tonnes in 1960, 50,804 tonnes in 1970, 43,740 tonnes in 1980, 34,055 tonnes in 1990, 32,363 tonnes in 1993, 23,723 tonnes in 1995, and 32,323 tonnes in 1999. The usage of endosulphan has increased with the prohibition of organochlorine pesticides, which have a high persistence and a number of ecotoxicological side effects in Turkey, reaching 327 tonnes in 1987 [1, 2].

1.2. *Import and export*

The amount of organochlorine pesticides imported has increased to 35,900 kg in 1999, while it was 2000 kg in 1996. The production amount, therefore, has decreased to 42,171 kg in 1999, while it was 723,380 kg in 1996. According to official records, all of these pesticides are endosulphan preparations. However, DDT, toxophene, and BHC are still being imported illegally. Furthermore, BHC has been used against human and animal parasites between 1990 and 1995 [1].

Various preparations of endosulphan, which has been imported as 22 tonnes of active ingredient, have been used since 1988. The consumption amount of endosulphan preparations are as follows: 765 tonnes in 1988, 560 tonnes in 1989, 614 tonnes in 1990, 774 tonnes in 1991, 1635 tonnes in 1992, 447 tonnes in 1995, 829 tonnes in 1996, 1136 tonnes in 1998, and 922 tonnes in 1999. The import and export rates of pesticides in Turkey are given in tables 4 and 5, respectively. The majority of countries, from which Turkey import pesticides, are in the European Union [1, 2].

Table 5. Amount (tonnes) of imported pesticides in Turkey for different years.

Groups	1995	1996	1997	1998	1999
Insecticide	2008	2635	2626	3146	1879
Acaricide	321	326	105	116	49
Fumigants and nematocides	1285	1203	1594	1807	1590
Fungicides	1158	1932	1604	1370	1794
Herbicides	1153	1361	1306	1887	1763
Others	366	275	312	1037	812
Total	6291	7732	7547	9363	7887

2. Residue studies in various environment and organisms in Turkey (1980–2004)

The pesticide residue analyses were carried out in samples of fresh water, sediment, sea water, crab, mussels and fish, soils, human and animal milk, butter, and human adipose tissues.

2.1. *Terrestrial habitats*

The analyses were carried out in samples of various soils from different parts in the Göksu Delta. Pesticide residues were analysed via gas chromatography by using a Ni63 electron capture detector. As a result of the study, 13 organochlorine pesticides and their residues were detected in various parts of the Göksu Delta (residues ranging from 0.013 $mg\,kg^{-1}$ of lindane in non-agricultural soils to 5.416 $mg\,kg^{-1}$ of pp′-DDE in soils). Organochlorine pesticide concentrations in soil samples from agricultural areas were generally higher than in water and sediment. α-BHC, aldrin, heptachlor, op′-DDT, op′-DDD, and pp′-DDE were detected at high levels in agricultural soil samples [3].

2.2. *Food*

Residues of organochlorine pesticides were detected in milk produced in the Çukurova region of Turkey between May and November, 1974. Pesticide residues were analysed via gas chromatography by using a Ni63 electron capture detector. The residues found in order of importance were lindane, aldrin, heptachlor, dieldrin, DDT, and endosulphan, respectively. The pesticide residue levels in milk samples, even in minimal amounts, were well above the tolerance values accepted in European countries. Seasonal changes were observed in residue levels [4].

Organochlorine pesticide residues in commercial milk from different regions of Turkey were investigated, and α-BHC, β-BHC, δ-BHC, DDT, and its metabolites were found [5]. Some organochlorine pesticide residues were investigated in cow's milk in Kayseri-Turkey ($n = 24$). Almost all samples contained organochlorine pesticide residues. The most frequently detected compounds were DDT and its metabolites, α-BHC, β-BHC, and δ-BHC (lindane) [6]. Furthermore, aldrin, dieldrin, and endosulphan were also found in the samples. Ninety-one percent of the milk samples were found to be contaminated. Endrin was found in only two samples, while 87% of the samples were contaminated by one or more BHC isomers. Twenty-six percent of the organochlorine pesticides comprised DDT and its metabolites [7].

The percentage of organochlorine pesticides was studied in tea plants grown in Turkey, Russia, China, India, and Sri Lanka. The major pesticides were α-HCH, β-HCH, δ-HCH, DDT, and their metabolites. Compared with other countries, Turkish teas contained 29% fewer pesticides [8].

Another study has been conducted to examine organochlorinated compounds in Turkish tea samples from the Eastern Black Sea region. The content of 16 PAHs, six PCBs, 16 organochlorine pesticides, HCB, Quintocene, endrin, op-DDT, and pp-DDT were found at detectable levels as a result of this investigation [9].

Organochlorine pesticide residue analyses had been conducted on honey and pollen. Honey and pollen samples were taken from beehives exposed to chemical application during September 2000. Extracts obtained for organochlorine (OC) pesticides were analysed for 13 OC residues including α- and β-BHC, lindane, aldrin, dieldrin, endrin, DDT, and its derivatives pp′-DDT, op′-DDD, op′-DDT, op′-DDE, and pp′-DDE, heptachlor, and heptachlor epoxide via gas chromatography analysis conducted using a Ni electron capture detector. Residues of DDT and its derivatives, as well as residues of aldrin and its metabolites endrin and dieldrin were detected in six out of 16 honey samples and in two out of eight pollen samples. The detected residues were in $\mu g\,kg^{-1}$ concentrations and below the level of toxicity. According to the data obtained, one pollen sample was found to have more kinds of pesticide than the honey. This indicates that the OC pesticides used during the blooming season in these areas, where the honeybees wander about, had infected the pollens and plants. As a result, these pesticides and their metabolites are still present in honey and pollen because of their persistence, although they are no longer used [10].

Another study has been conducted to examine the OC pesticide residue levels of Quintozene (PCNB), pp′-DDT, pp′-DDE, and pp′-DDD in butter and cracked wheat sold in local markets in Ankara. The use of some pesticides is restricted so as to prevent environmental pollution and for the well-being of consumers. Therefore, the study aimed to analyse the results achieved as a result of such restrictions. A hundred butter samples and 50 cracked wheat samples were obtained from different markets for analysis. The results of this study revealed that the butter sold in local markets in Ankara did not contain OC pesticide residues, while the cracked wheat contained PCNB and lindane residues, although the levels determined were within the tolerance limits designated by the Food and Agriculture Organization (FAO) [11].

An overview has focused on the contamination levels of fish from Turkish waters by selected OC pesticides, nitromusks, and chlorobiphenyl congeners. The fish species tested have been demonstrated to contain particularly unmistakable amounts of OC pesticides, prior to processing for canned products that would be brought to the market. Sardines, sardelles, and trout showed results generally far below the German regulatory limits. However, the total amount of DDT in pelamides reached an order of magnitude near the German limit of $0.5\,mg\,kg^{-1}$ (based on wet weight) [12].

2.3. *Levels in humans*

OC pesticide residues and polychlorinated biphenyl (PCB) concentrations were determined in adipose tissue from 34 infants, 14 two-year-old children, and two other children. The highest mean concentration detected during the first 2 years of life was for PCBs ($0.67\,mg\,kg^{-1}$), followed by DDT ($0.57\,mg\,kg^{-1}$), HCB ($0.23\,mg\,kg^{-1}$), and HCH ($0.15\,mg\,kg^{-1}$). Concentrations of HCB and PCB, which are especially characteristic for highly industrialized countries, were considerably higher in the children of German mothers than in those of Turkish mothers. All single investigated values were lower than the mean values for adults in Germany, but many were still higher than the mean concentrations for adults in other parts of the world. Studies on breakdown in children with a high intake of mother's milk and those with a lower intake showed a highly significant association with the quantity of mother's milk consumed: the concentration of organohalogens in adipose tissue of children with high intake was significantly higher than in those with a lower intake. The possible pathogenetic effects of these organohalogens on the health of children have been thoroughly studied [13]. OC pesticides in human milk were determined. The most common residues found in the samples were pp′-DDT, pp′-DDE, op′-DDT, α-BHC, and lindane. Aldrin and methoxychlor had not been detected in any of the 80 samples [14].

Analyses of adipose tissues collected during surgical operations in Turkey showed that the residues of HCB, β-BHC, pp′-DDE, pp′-DDT, and heptachlor epoxide, which are the major OC pesticide contaminants, were higher in females than in males and increased with age in both sexes. The concentrations of pp′-DDE and pp′-DDT in human adipose tissues in Turkey were lower than the samples collected in Italy and Spain, and showed a downward trend when compared with previous studies [15, 16]. pp′-DDT, op′-DDT, pp-DDE, HCH, BHC, and its main isomers including α-, β-, δ-BHC, aldrin, and its metabolite dieldrin, heptachlor, heptachlor epoxide were investigated in 51 samples of breast milk from 51 lactating women in 1988. The ages of mothers who worked in businesses related to agriculture, ranged from 17 to 33 years (mean 24.2 years). The concentrations of heptachlor, heptachlor epoxide, benzene hexachloride (α-BHC, β-BHC, δ-BHC), aldrin, pp′-DDE, dieldrin, op′-DDT, and pp′-DDT were measured via gas chromatography and were found to be 84 ± 23, 96 ± 20, 522 ± 120, 156 ± 20, 198 ± 130, 47 ± 9, 11 ± 4, 2389 ± 280, 6.7 ± 3, 70 ± 12, and $410 \pm 60\,\mu g\,kg^{-1}$ in milk and fat, respectively. The concentrations of chlorinated pesticides in human milk samples from the Kayseri region were compared with similar data obtained from other countries. The amounts of total BHC and aldrin derivatives were below the acceptable daily intake (ADI) limits, whereas the amount of total DDT derivatives was above the limits designated by the World Health Organization (WHO) [17].

2.4. *Fresh water and biota*

The analyses were carried out in samples of various organisms from different environments in the Göksu Delta. As a result of the study, 13 OC pesticides residues were detected in various parts of the Göksu Delta. OC concentrations in soil samples from agricultural areas were generally higher than in water and sediment. α-BHC, aldrin, heptachlor, op′-DDT, op′-DDD, and pp′-DDE were detected at higher levels in soil samples than in water and sediment. In fish, the OC concentrations were detected in varying amounts in different species and tissues. There were differences in OC concentrations in carp and grey mullet. In carp, six different OC pesticide residues in liver and 13 different OC pesticide residues in adipose tissue were detected (mean concentrations ranging from $1.072\,mg\,kg^{-1}$ endrin to $4.217\,mg\,kg^{-1}$ op′-DDT). In grey mullet, however, six different OC residues in liver and 11 different OC pesticide residues in adipose tissue were detected (mean concentrations ranging from $0.066\,mg\,kg^{-1}$ of pp′-DDE to $0.912\,mg\,kg^{-1}$ of op′-DDT). Aldrin was found in greater concentrations than dieldrin in blue crab, carp, and grey mullet adipose tissues. Also, heptachlor was found in greater concentrations than heptachlor epoxide in carp adipose tissue and grey mullet liver. OC pesticide accumulation in carp was higher than in grey mullet. Chosen species of water birds and their eggs were contaminated by OC pesticide residues. OC pesticide concentrations varied among bird species and their eggs. The concentrations were higher in adipose tissue than in the liver of water birds. In coots, four, thirteen, and nine different OC pesticide residues were detected in liver, adipose tissue, and eggs, respectively (mean concentrations ranging from 0.075 $mg\,kg^{-1}$ op′-DDT in eggs to 2.147 $mg\,kg^{-1}$ β-BHC in adipose tissues). In mallards, five, twelve, and five different OC pesticide residues were detected in liver, adipose tissue, and eggs, respectively (mean concentrations ranging from 0.046 $mg\,kg^{-1}$ pp′-DDE in adipose tissue to 2.775 $mg\,kg^{-1}$ β-BHC in adipose tissues). Thirteen different OC pesticide residues were detected in small egrets' eggs (mean concentrations ranging from 0.045 $mg\,kg^{-1}$ endrin to 1.789 $mg\,kg^{-1}$ pp′-DDE in small egrets) [3].

OC pesticide residues were detected in sediment and water samples taken from nine different stations in Manyas Lake-Balıkesir (known as the 'bird paradise') and its basin during November 1996 and May 1997. According to the results of residue analysis, ecosystems were found to be contaminated by OC pesticide residues. The residues consisted mainly of heptachlor, heptachlor epoxide, HCH, aldrin, op′-DDT, op′-DDE, endrin, and dieldrin. The contamination level was higher in the lake than in the surrounding freshwaters. These pesticides were not found at a toxic level in water samples, but heptachlor and heptachlor epoxide in sediments may be toxic for water birds and for organisms living in the deeper waters [18].

Pesticides and PCBs were measured in 42 sources, including rivers and streams in industrial and domestic discharge points along the Turkish Black Sea Cost in three seasons of the year 1993 [19]. Concentrations of 11 pesticides and PCBs including lindane, heptachlor, heptachlorpoxide, aldrin, dieldrin, endrin, pp′-DDE, op′-DDE, op′-DDD, op′-DDT, and pp′-DDT were also measured. Concentrations of measured chlorinated compounds in some of the rivers and streams were below the detection limits. However, concentrations of heptachlor and aldrin were below the detection limit in one or more of the major rivers.

Five different OC pesticides and their degradation products were detected in sediment, water, and fish in the upper Sakarya basin. In fish samples, DDT and its metabolites pp′-DDE, op′-DDT, pp′-DDT, pp′-DDD, and op′-DDD (mean concentrations 2.454, 1.74, 1.474, 1.262, and 1.199 $\mu g\,g^{-1}$, respectively) were detected at high levels in October. Heptachlor epoxide, the degradation product, was found to be greater in adipose tissue during the same month (mean concentration 3.635 $\mu g\,g^{-1}$). The bioconcentration factors of these pesticides have also been estimated. In the study, all OC pesticide residues were detected at higher degrees at stations, which are exposed to various pollutants including effluent discharge from plants, industrial and agricultural wastes. Dieldrin levels were higher than aldrin, and heptachlor epoxide levels were higher than heptachlor [20].

The OC pesticide residues were analysed by means of gas chromatography in water, sediment, plankton, crab, and fish samples collected during the field surveys in the Köyceğiz Lagoon System between October 1992 and February 1994. No OC pesticide residues were detected in water and plankton samples. Five OC pesticide residues were detected in sediment samples. The total DDT and dieldrin residues were not found in all sediment samples, but α- and β-HCH were detected in all station samples. The highest residue among these was detected in the first station and the lowest in the fourth station. δ-HCH was found only in sediment samples collected from the first station. Aldrin was detected in the first and second stations, while dieldrin was detected in the first and third stations. Small amounts of α-HCB, β-HCH, δ-HCH, aldrin, and endrin, from the group of OC pesticides were detected in crab samples. Common carp had the widest range of pesticide residues and the highest mean of endrin ($36\,\mu g\,kg^{-1}$). The mean endrin residue levels for three fish species in the Köyceğiz Lagoon System ranged between 1 and $36\,\mu g\,kg^{-1}$. DDT, dieldrin, α-HCH, and β-HCH were found only in common carp (*Cyprinus carpio*) and mosquito fish (*Gambusia affinis*) samples. The number of OC pesticides and the residue levels detected in common carp and mosquito fish samples were higher than in mullet samples. The residue levels in mosquito fish samples may have represented the actual pesticide levels in the aquatic system more accurately, since mosquito fish were widespread and more abundant than the other sampled fish species. None of the samples had residue levels above the extraneous residue limits (ERC) and acceptable daily intake (ADI) for the respective pesticides, set by the FAO/WHO Codex Alimentary Commission. This indicates that the residue levels were within the acceptable OC pesticide residue limits in fish for human consumption. The highest and lowest concentrations observed were δ-HCH ($2.60\,\mu g\,kg^{-1}$) and aldrin ($0.42\,\mu g\,kg^{-1}$), respectively, in crab tissues. The order of OC quantities followed δ-HCH > endrin > β-HCH > α-HCH > aldrin. DDT, dieldrin, α-HCH, β-HCH, δ-HCH, aldrin, and endrin were detected in fish muscle tissues. The concentration of OC pesticides mostly followed the order β-HCH > α-HCH > aldrin > δ-HCH > endrin. DDT, dieldrin, α-HCH, β-HCH, δ-HCH, aldrin, and endrin were detected in fish muscle tissues. As a result, 61.11% of the samples were positive for one or more of the pesticide residues. δ-HCH, aldrin, and endrin were detected in all fish samples analysed [21].

A positive result was obtained for at least one of the pesticide residues in each fish species. Presences of β-HCH and δ-HCH were observed in all analysed fish samples. *Liza ramada* had the widest range of pesticide residues and the highest mean of endrin ($57\,\mu g\,kg^{-1}$). The residue levels were greater in samples of *Oreochromis mossambica* (except endrin) than in the other fish species. The OC residue level was lower in blue crab tissues than in fish tissues. The invertebrates then act as the first link in the aquatic food chain and mediate transport to predatory fish species. Similar results have been observed in crab and fish samples from the Göksu Delta. The OC residue levels detected in fish tissue samples were lower than the reported results. The results of this study show that the Köyceğiz Lagoon System is contaminated with low levels of OC pesticides [22].

The concentrations of nine OC pesticide residues in water resources and tap waters of Istanbul, Turkey were determined via gas chromatographic methods following the enrichment through adsorption and elution techniques. The observed OC pesticides were α-HCH, δ-HCH, and aldrin, which have been prohibited from usage. The contents of α- and δ-HCH in raw waters were within the range of 0.34–$1.7\,\mu g\,L^{-1}$, and not detected to $0.077\,\mu g\,L^{-1}$, respectively. Aldrin was observed at a concentration of $0.03\,\mu g\,L^{-1}$ in some of the samples. The residue levels of OC pesticides in drinking water supplies of Istanbul were found to be significantly below the maximum permissible level of standards. The effectiveness of portable water-treatment processes and the importance of maintenance and backwashing of sand filters in pesticide removal was observed. Improper and delayed backwashing of filters caused an increase in pesticide residues in the distributed water. In older water-distribution lines, some of the OC pesticides were also observed in higher concentrations [23].

Water, sediment, and various fish species sampled at different localities in Sarıyar Dam Lake were analysed for determining OC pesticide levels. OC pesticide concentrations in water and sediment of running-water systems and lake environments, and OC pesticide concentrations in fish were determined. Eleven different pesticides and their residues were detected in water samples from selected stations of Sarıyar Dam Lake (ranging from 0.011 mg L^{-1} pp′-DDT in Sarıyar Station to 0.069 mg L^{-1} pp′-DDT in Çayırhan station). The highest amount of OC residues in sediments, among seven stations, was determined in Uşakbükü Station (11 different types of OC residues; maximum concentration 0.708 mg kg^{-1}), and, as in the case of water, levels observed in the Aladağ Creek seemed to be the lowest (only lindane; 0.018 mg kg^{-1}). The types and levels of OC pesticide residues were determined in fish species (bleak, carp, and eels) caught at four stations located in Sarıyar Dam Lake. The residue levels in bleak were lower than the other two fish species (carp and eels) studied. Six types of OC pesticide residues (α-BHC, β-BHC, op′-DDT, pp′-DDT, op′-DDD, and op′-DDE) were determined in adipose tissue from the bleak samples caught at Aladağ Creek, Çayırhan, Uşakbükü, and Sarıyar stations. The highest OC pesticide concentration was observed in the samples from Uşakbükü Station (0.137 mg kg^{-1}; op′-DDE). On the other hand, only op′-DDE was found in the samples taken from the station in Aladağ Creek with a concentration of 0.012 mg kg^{-1}. The bioaccumulation rates have been estimated for all fish species studied. In particular, DDT and its degradation products, and heptachlor epoxide were found to have accumulated in fish tissues. Furthermore, op′-DDE was the residue with the highest bioaccumulation. The bioaccumulation rates estimated for op′-DDE in bleak, carp and eels were 12.6, 18.4, and 88.6, respectively. In eels, accumulation rates especially of DDT and its degradation products were high. In addition to these, heptachlor epoxide, α-BHC, and β-BHC also had considerable bioaccumulation levels [24].

A total of 13 OC pesticide residues have been determined in water and sediment in Tuz, lake, Hirfanlı Dam lake, Eşmekaya lake, Tersakan lake, and Bolluk lake in Central Anatolia. α-BHC, β-BHC, heptachlor epoxide, aldrin, op′-DDT, op′-DDD, and pp′-DDT were detected in high levels in sediment samples. In Tuz lake, Hirfanlı Dam lake, Eşmekaya lake, Tersakan lake, Kozanlı lake, and Kulu lake, OC pesticide residues (especially α-BHC, β-BHC, aldrin, dieldrin, heptachlor epoxide, and DDT metabolites op′-DDT, pp′-DDT, and pp′-DDD) in water and sediment samples were generally higher than in other lakes, because they are located in wide agricultural areas. The highest amount of extractable α-BHC was 1.38 µg g^{-1} (range not detected to 2.719 µg g^{-1} mean) which was found in the sediment sample of Bolluk Lake. The highest residue level of heptachlor epoxide was 1.398 µg g^{-1} which was found in sediment samples of Kozanlı Lake. Also, the highest average amount of extractable β-BHC (2.328 µg g^{-1} mean of Hirfanlı Lake dam) was detected in sediment samples. DDT and its metabolites pp′-DDE, op′-DDD, op′-DDT, pp′-DDD, pp′-DDT (mean concentrations 1.421, 1.389, 2.244, and 0.969 µg g^{-1} in Tuz lake, Hirfanlı dam lake, and Tuz lake, respectively) were detected at high levels in sediment samples. These high residue levels of pesticides may be due to continuous usage of OC pesticides [25].

Water, sediment, and fish species (*Cyprinus caprio*) sampled at different localities in Meriç Delta were analysed for determining 21 OC pesticide levels. The analysed water samples showed the presence of the following OC pesticide residues at concentrations

Table 6. Embryotoxic, teratogenic effects, and hatching success of heptachlor and o,p′-DDT for domestic hens (*Gallus gallus domesticus*) and ducks (*Anas platyrynchos*).

	Control		Aceton control		o,p′-DDT		Heptachlor	
Groups	Ducks	Hens	Ducks	Hens	Ducks	Hens	Ducks	Hens
Hatching success (%)	83.3	70.6	77.8	68.4	32.4	48.6	46.3	59.4
Early embryo death (%)	0	5.3	12.5	11.1	32.5	16.3	40.5	24.4
Late embryo death	5.9	10.5	18.7	22.2	45.0	27.9	50.0	51.2
Total embryo deaths	5.9	15.8	31.2	33.2	77.5	44.2	90.5	75.6
Alive embryo	94.1	84.1	68.7	66.7	22.45	55.8	9.5	24.4
Malformations								
Fore-limb and hind-limb defects (%)	5.6	0.0	11.1	0.0	10.8	5.1	19.5	2.7
Large defects (%)	0.0	0.0	0.0	0.0	18.3	7.7	9.7	13.5
Microphytalmia-Aphytalmia (%)	0.0	0.0	5.6	5.3	10.8	5.1	14.6	8.1
Oedemas (%)	16.7	5.9	11.1	15.8	45.9	7.7	46.3	5.4
Open abdomen (%)	5.6	5.9	11.1	10.5	32.4	38.5	26.8	24.3

of OC pesticides ranging from 0.054 to 1.127 $\mu g\,L^{-1}$ for Σ HCHs, 0.023 to 0.786 $\mu g\,L^{-1}$ for Σ heptachlor, 0.012 to 0.028 for aldrin, 0.127 to 0.2 for Σ chlordane, 0.091 to 1.66 for Σ endosulphan, 0.308 to 1.0 for Σ DDT, not detected to 0.01 for dieldrin, and 0.047 to 0.617 for Σ endrin. In water samples, endrin aldehyde and methoxychlor residues were not found in any stations.

Among the analysed OC pesticides, residue levels in sediment samples ranged from 0.406 to 3.243 for Σ HCH, 0.113 to 2.033 for heptachlor, 0.207 to 1.473 for aldrin, 0.063 to 1.103 for Σ chlordane, 0.87 to 2.333 for Σ endsulphan, 0.524 to 4.036 for Σ DDT, 0.007 to 0.650 for dieldrin and 0.597 to 2.127 for Σ endrin. Methoxychlor residues were not found in any station. Concentrations of OC pesticides in fish samples ranged from 725.57 to 1470.055 $ng\,g^{-1}$ for Σ HCH, 3.04 to 5.4 $ng\,g^{-1}$ for Σ heptachlor, 85 to 43.81 $ng\,g^{-1}$ for Σ chlordane, 28.34 to 86.02 $ng\,g^{-1}$ for Σ endosulphan, 6.14 to 62.25 $ng\,g^{-1}$ for Σ DDT, 1.35 to 17.78 $ng\,g^{-1}$ for dieldrin, 29.5 to 126.98 $ng\,g^{-1}$ for Σ endrin, and 5.79 to 50.93 $ng\,g^{-1}$ for methoxychlor. We have analysed the distribution characteristics of individual OC pesticide components and found that α-, β-HCH, DDE, β-endosulphan, heptachlor epoxide, and endrin ketone were the most common OC pesticide contaminants in Meriç Delta [26].

2.5. *Marine environment and biota*

Residues of DDE, DDT, and PCBs were detected in four different bony marine fish species: grey mullet, red mullet, striped mullet, and gold bandgoat fish, as well as in shrimp, limpet, and sediment samples obtained from the Eastern Mediterranean Coasts of Turkey. The PCB levels in living organisms and sediments were very low, and below the detection limits in most cases. The DDE and DDT values were relatively high when compared with PCBs, and there was no linear correlation between the OC pesticide residue concentrations and the extractable organic material of the analysed samples [27].

The residue levels of OC pesticides were detected in various marine fish species along the Turkish Aegean coastline between Güllük Bay and Saros Bay. A total of 266 fish samples were analysed between February 1979 and February 1980.

The ratios of incidence of the residue types were as folows: BHC 100%, DDT 98.5%, aldrin 95.5%, dieldrin 90%, and endrin 71.1%. The highest residue content ($0.108\,mg\,kg^{-1}$) was found in fish samples from Ayvalık Bay. Residue concentrations increased as a function of age and from spring to winter. The mean concentration of insecticide residues (wet tissue basis) was $0.015\,mg\,kg^{-1}$ [28]. The concentrations of OC pesticide residues in the Eastern Aegean Sea were studied for the composition of DDT, and its metabolites were generally in the order of pp′-DDE (46%), pp′-DDD (34%), pp′-DDT (16%), and op′-DDT (4%). Concentrations of DDE and DDD ranged between 10 and 18, and between 0.86 and $4.5\,\mu g\,kg^{-1}$ (wet wt), respectively, in *Mullus barbatus*. The levels of aldrin varied between 0.10 and $0.61\,\mu g\,kg^{-1}$ in samples from the Eastern Aegean Sea. Lipid content (the extractable organic matter with hexane) determined with the aid of soxhlet extraction of samples with hexane was found to be 1.2–1.4% and 4.2–6.5% in May and September, respectively. Other OC pesticides (op′-DDT, pp′-DDT, heptachlor, endosulphan, dieldrin, lindane, and endrin) were below the detection limit of $0.10\,\mu g\,kg^{-1}$ (wet wt). Fish lipid content can substantially influence the bioaccumulation of organochlorinated compounds. A positive relationship was apparent between lipid content and OC concentrations during sampling periods. PCBs were not detected in *Mullus barbatus* analysed under the experimental conditions. In the eastern Mediterranean, evaporation exceeds precipitation, and therefore the co-distillation of PCBs is also possible in the Aegean Sea [28].

Polycyclic aromatic hydrocarbon (PAHs) and OC pesticide (DDT and its derivatives HCB, HCH, heptachlor, heptachlor epoxide, aldrin, and dieldrin) levels have been studied in mussels (*Mytilus galloprovincialis*). Mussel samples collected from Trabzon, Sinop, and Istanbul during July 1989 to April 1990 have been separated into two size groups. PAHs were analysed by using the flourimetric method, and OC pesticides via gas chromatography. PAH levels in mussels showed seasonal and regional variations. The lowest PAH level was determined in Sinop ($9.6\,mg\,kg^{-1}$), while PAH levels measured in Trabzon and Istanbul were 21.7 and $22\,mg\,kg^{-1}$, respectively. Total DDT concentrations varied between 17 and $52\,\mu g\,kg^{-1}$, while total HCH changes varied between 0.5 and $24\,\mu g\,kg^{-1}$. The total DDT concentration was high as a result of the high pp′-DDE levels. pp′-DDE was determined in mussels of all size ranges in all regions. Although the changes were more or less the same, seasonal changes in the OC pesticide levels varied significantly. HCB and DDT concentrations reached the lowest levels in spring [29].

Chlorinated pesticides and PCBs were measured in the mussel *Mytilus galloprovincialis* and in sea water at six sapling points between Yalıköy (Ordu) and Sinop in 1999–2000. In mussel samples, the most common pollutants were DDT (max. $1800\,pg\,g^{-1}$ ww, min. $240\,pg\,g^{-1}$ ww) and its metabolites DDD (max. $540\,pg\,g^{-1}$ ww, min. $240\,pg\,g^{-1}$ ww) and DDE (max. $2800\,pg\,g^{-1}$ ww, min. $70\,pg\,g^{-1}$ ww). Dieldrin, heptachlor, and HCB were notable contaminated mussel samples. PCBs were determined in none of the biota or seawater samples [30].

3. Toxic effects on the environment and the biota

Toxic substances cause acute, sub-chronic, and chronic effects on living organisms in the environment. Chronic effects are especially caused by long-term exposure against lipid-soluble toxic substances at lower doses. The effects of such substances may be classified as mutagenic, histopathological effects, enzyme-inducing and/or -inhibiting, carcinogenic, and teratogenic. As a result of these effects, individuals may be affected in short durations, while the long-term outcome is an impact on populations and community.

Manyas Lake is contaminated by different types of pesticides. The residues consisted mainly of heptachlor, heptachlor epoxide, HCH, aldrin, op′-DDT, op′-DDE, endrin, and dieldrin. The contamination level was higher in the lake than in the surrounding freshwaters. These pesticides were not found on a toxic level in water samples, but heptachlor and heptachlor epoxide in sediments may be toxic for water birds and for organisms living in the deep. These pesticides obviously affect water birds, too. The effects include a decrease in egg production and hatching success, an increase in hatchling mortality, and malformations in hatchlings. The contamination level of the water is above the threshold toxic level for aquatic fauna and flora, when compared with Turkish regulations [18].

In particular, OC pesticides have been found to be effective as a result of the overall studies on the mutagenic, histopathological, enzyme inducing, and/or inhibiting, and teratogenic effects of agricultural and industrial PTSs. Agricultural application doses of DDT, BHC, and heptachlor were found to be teratogenic on chicken embryos when applied with the agricultural application dose and method on the fertilized eggs. This effect is characterized mostly by skeletal deformations, microphytalmia, and aphytalmia related to the dose [31]. An increase in the activity of acid phosphatase, which plays an important role during the embryonic development, has been observed in fertilized eggs treated with linden when compared with the control groups [32].

Aldrin, endosulphan, heptachlor, and tetradifon were found to be mutagenic, as determined from the AMES testing method. It has been found that endosulphan has a mutagenic effect on *Salmonella typhimurium* TA98 and TA100 strains. Among these, mutagenic effects of endosulphan were observed in higher concentrations compared with the others at doses of 10, 100, 1000, and 2000 $\mu g\,plate^{-1}$ and varied among strains. Aldrin, heptachlor, and tetradifon were weakly mutagenic on *S. typhimurium* TA100 [33]. Endosulphan is effective on DNA synthesis in mice fibroblast cultures.

Mixed cultures of micro-organisms isolated from agricultural soils in the Aegean and Marmara Regions of Turkey were used to degrade endosulphan. Toxic effects of endosulphan itself and its degraded metabolites were compared in mice, and degraded products were found to be non-toxic. This result indicates that endosulphan breaks down in soil, resulting in a significant decrease in its toxic effect. The original form of endosulphan causes histopathologic effects in liver and kidneys. A reduction in endosulphan in waters via ozone oxidation has been shown in the study. Endosulphan also has an effect on the α-amylase activity in *Gambusia affinis*, a mosquito-predatory fish species [34].

Heptachlor and o,p′-DDT residues were determined in eggs collected in nests in the Göksu Delta and then the same amounts were applied to the fertilized hen and duck eggs for investigating hatching success, embryotoxic and teratogenic effects. Some developmental abnormalities were found, and these are shown in table 16 [35].

In recent years, studies have been conducted on the activation of PTSs and Cyt P450 mono-oxygenase enzymes in indicator fish species. One of these studies has been conducted on bottom-feeding fish that live in the Izmir Bay. The outcomes showed a significant decrease in the EROD activity in fish (mullet and the benthic fish common sole are used as biomarkers for PAHs and PCB-type pollutant) that have been harvested (catching) from six different stations along the Bay from the city borders towards the inner parts of the Aegean Sea [36]. The effects of OC pesticides have been determined in another study in Sarıyar Dam Lake. An increase in EROD activity has been determined in fish living in the environment, where DDT, heptachlor epoxide, aldrin, and dieldrin have been detected [24].

Micro-organisms in the soil and some saprophyte fungi detoxify chlorinated hydrocarbons by dechlorinating them. Therefore, the toxicity of such substances that infect the soil decreases gradually. In a study carried out by Arısoy and Kolankaya [37], pp′-DDT, heptachlor, endosulphan, and lindane have been shown to cause biodegradation in *in vitro* cultures of white-rot fungi strain and *Plerutous sajor cajo*. The toxicity of degraded metabolites of these insecticides, for which the CL amounts have reduced, decreased consequently, and toxic effects have also decreased in mice when CL was removed [38].

4. Conclusion

This review focuses on pesticides used in Turkey and organochlorinated residues in samples of various organisms and different environments obtained from the Black Sea, Central Anatolia, the Aegean, and the Mediterranean regions of Turkey. Some example studies have also been given for land water systems including Göksu Delta, Manyas Lake, Sakarya basin, Sarıyar Dam Lake, some lakes of Central Anatolia, and the Köyceğiz Lagoon System. OC pesticials residue in human milk and adipose tissue, as well as in cow milk and butter, honeybee products, and fish sold in markets have been demonstrated in a number of studies conducted in different years. In particular, DDT and its metabolites, HCH isomers aldrin and dieldrin, heptachlor epoxide, and endosulphan residues were detected, all below toxic levels for humans. There is a strong neccesity for investigating the environment and biota in other parts of Turkey which are exposed to agricultural activities. The neccesity for enhanced systematic measurements for monitoring pollutants in food chain affecting the water, soil, and bio-indicator organisms thus becomes evident.

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