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The Organochlorine Pesticide Residues in the Drinking Waters of Afyonkarahisar, Turkey

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Abstract

The Organochlorine pesticide residues in the drinking waters of the Afyonkarahisar province of Turkey were investigated. The study was based on 72 specimens collected from twelve stations, wells, and advancement centers, between 2006-2007. In the study of the pesticides, liquid-liquid extractions were carried out and GC-ECD was performed. In total, eighteen different pesticides were detected. ß-HCH, 4,4'-DDT, endrin keton and methoxychlor (0.281, 0.138, 0.120, 0.102 μg/l, respectively) concentrations were found to be higher than the acceptable limits of EC, the drinking water quality standard in some period between 2006-2007. Aldrin, α-HCH, δ-HCH, endosulfan sulfate, heptachlor epoxide, and α-endosulfan levels were found to be in trace amount.

Keywords: Afyonkarahisar, drinking waters, GC, organochlorine pesticides, Turkey.

Afyonkarahisar İçme Sularındaki Organoklorlu Pestisit Kalıntıları

Özet

Afyonkarahisar ili içme sularındaki organoklorlu pestisit kalıntıları araştırılmıştır. Çalışma, 2006-2007 tarihleri arasında kuyu ve terfi merkezi olan 12 istasyondan toplanan 72 örnekte yapılmıştır. Pestisitler sıvı-sıvı ekstraksiyonla elde edilmiş ve GC-ECD'de okunmuştur. Toplam olarak 18 farklı pestisit belirlenmiştir. ß-HCH, 4,4'-DDT, endrin keton ve metoksiklor konsantrasyonları 2006-2007 arasında bazı periyotlarda içme suyu kalite standartlarında EC'nin kabul edilebilir sınırlarından daha yüksek bulunmuştur (sırasıyla, 0.281, 0.138, 0.120, 0.102 μg/l). Aldrin, α-HCH, δ-HCH, endosülfan sülfat, heptaklor epoksit, ve α-endosülfan seviyelerinin iz miktarda olduğu görülmüştür.

Anahtar Kelimeler: Afyonkarahisar, GC, içme suyu, organoklorlu pestisitler.

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INTRODUCTION

Several hundred pesticides of different chemical compositions are currently used for agricultural and vector control purposes all over the world (Rajendran et al. 2005). Because of their extensive use, they are detected in various environmental matrices, such as soil, water, and air (Zulin et al. 2002). Due to their lipophilic nature, hydrophobicity, and low chemical and biological degradation rates, organochlorine pesticides (OCPs) have led to their accumulation in the biological tissues and subsequent magnification of concentrations in the organisms due to the progression up the food chain (Hernandez-Romero et al. 2004).

Developed countries have banned many organochlorine pesticides because of their potential toxic effects to man and their impacts on the ecosystems. In developing countries, however, organochlorine pesticides still remain the cheapest to produce and for some purposes, remain highly effective. Developing countries maintain that they cannot afford for reasons of cost and/or efficacy, to ban certain older pesticides. Due to ecological impacts in countries of application, pesticides have been banned in developed countries (such as DDT, toxaphene, etc.) for many years, but they are still consistently found in remote areas such as the high arctic (Hung and Thieman 2002).

The Organochlorine pesticides group includes DDT (dichlorodiphenyl trichloroethane), methoxychlor, aldrin, dieldrin, chlordane, toxaphene, endrin, heptachlor, and lindane (gamma isomer of benzene hexachloride (BHC). These are trade names for closely related hydrocarbon compounds to which several chlorine atoms have been joined (Hung and Thieman 2002).

Tsipi and Hiskia (1996) performed a study and found 16 organochlorine pesticides and 3 triazines in the drinking waters of Athens, Greece.

Shukla et al. (2006) determined the levels of

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organochlorine pesticides in the ground water of Hyderabad City, which were taken from, the 28 domestic well supplies of the city. They reported that all their samples, that were analyzed were found to be contaminated with four pesticides i.e. DDT, ß-Endosulfan, α-Endosulfan, and Lindane and the concentrations of pesticides in the water samples were reported to be above their respective ADI values for mankind.

Galfinopoulos et al. (2003) studied the organochlorine pesticide contaminations in the surface water of northern Greece and found HCH isomers, aldrin, dieldrin and endosulfan frequently. They reported that the concentrations of these pesticides were found to be higher than that of the EC's acceptable levels. Our results showed a similarity to their findings with the respect to their concentration levels.

Chemicals that are applied in tropical and subtropical countries are transported over long distances by global circulation. Pesticide residues reach the aquatic environment through direct runoff, leaching, careless disposal of empty containers, equipment washings, etc. (Atamanalp and Yanık 2001).

Residues of OCPs were detected in almost all environmental compartments, including water bodies (Ayas et al. 1997), food (Tieyu et al. 2005), fish (Manirakiza et al. 2002), and milk (Martinez et al. 1997) as well as in human beings (Cerrillo et al. 2005).

Some reports indicated that residues of OCPs presented a higher degree than the acceptable level for drinking waters, surface waters, and underground waters of some towns of varied countries (Rovedatti et al. 2001).

Many important wetlands in Afyonkarahisar province have been contaminated by a variety of pesticides for a long time, and the use of OCPs has been prohibited since 1980. Due to their environmental persistence, these pollutants can cause contamination of surface water and ground water.

The aim of this work was to determine the contamination level of the both OCPs and their derivatives in the drinking water of Afyonkarahisar province, and to assess the potential health risks posed to the consumers.

MATERIALS AND METHODS

Study area

In this study, the residue levels of 18 organochlorine pesticides (OCPs) were found in the drinking water samples obtained from the different regions of Afyonkarahisar province. In total, 72 water samples, from 12 sampling sites, were collected every two months between June 2006 and April 2007. The sampling sites were composed of four main water supplying wells, two advancement centers, and six water mains and 10 of the stations are shown in Figure 1. Since Karamık (60 km away, SW) and Bolvadin boroughs (61 km away, SE) districts are far away from the center of the city they are not seen.

Sample collections

For this study, a total of 72 water samples from 12 sampling sites were collected. All the water samples were collected in high purity glass bottles and immediately transported to the laboratory. After this, the samples were stored at +4°C and extraction of the OCPs was performed within 48 h.

Chemicals and instrumentation

The solvents used for the extraction were methylene chloride and hexane obtained from Merck (>99.8% purity, HPLC grade for spectroscopy). The standard samples of the 18 pesticides were obtained from Dr. Ehrenstorfer GmbH, D-86199-Augsburg-Germany, with the purities of 97-99 %.

The qualitative and quantitative determinations of chlorinated pesticides were performed by using gas chromatography, HP Agilent 6890N series, with an electron capture detector (GC-ECD). This detector allows the detection of contaminants at trace level concentrations in the lower ppb range in the presence of a multitude of compounds extracted from the matrix to which these detectors do not respond. The column used for analysis was an HP-5-MS capillary column (30 m x 0.25 mm i.d. x 0.25 μm film thickness). Helium was used as the carrier gas for the system (75 Psi, 1 ml min^{-1}) used. Nitrogen was used as the makeup gas and the injection technique was in the splitless mode. The GC conditions used are seen in Table 1.

Analytical procedure

Liquid-liquid extraction followed by gas chromatographic detection (Anonymous 1989) was used for the determination of pesticide residues. A liquid-liquid extraction followed by GC-ECD was used to determine the organochlorine pesticides in the water samples. In general, the EPA protocols with certain modifications were used for the analysis. Around 1 l of the water sample was filtered using 0.45-Am Whatman glass fibre filter paper, treated

Table 1. The GC-ECD conditions.

Conditions	Values
Injector temperature	225 °C
Inlet pressure	7.00 psi
Detector temperature	320 °C
Oven programming	80 °C at 1 min
	80 °C -180 °C at 30 °C/min
	180 °C at 5 min
	180 °C -205 °C at 3 °C/min
	205 °C at 4 min
	205 °C -275 °C at 20 °C/min
	290 °C at 2 min
ECD makeup gas flow	60ml / min
Injection volume	1µl
Total run time	33 min

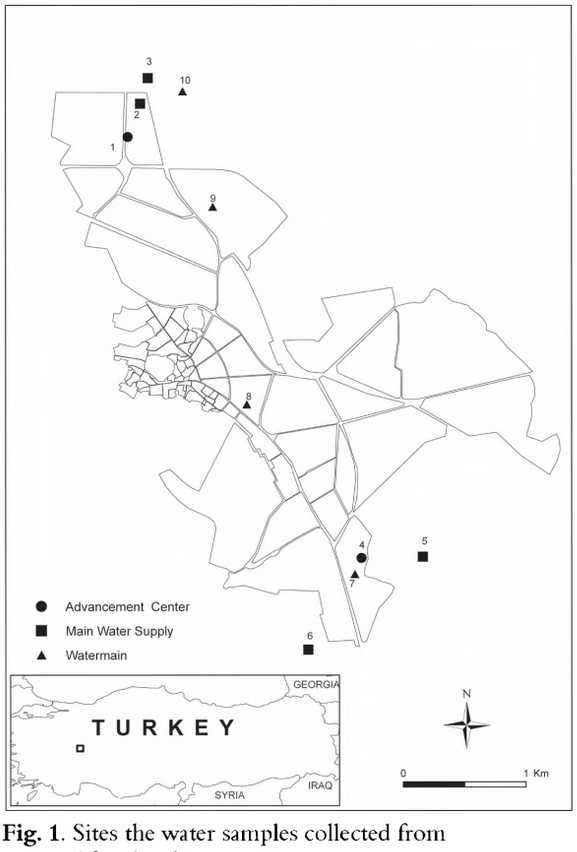

Fig. 1. Sites the water samples collected from Afyonkarahisar province

1- Çobanlar Advancement centre, 2- Çobanlar 7th Well , 3- Çobanlar 11th well, 4- Beşler Advancement center, 5- Beşler 7th well, 6- Bayraktepe well. 7- Ali İhsanpaşa districti, 8- Cumhuriyet district, 9- Karşıyaka district, 10- ANS Campus, 11- Karamık drinking water, 12-Bolvadin drinking water

with 10 g of sodium sulphate and extracted thrice with 60 ml of methylene chloride. The combined extracts were filtered and concentrated in a rotary evaporator. The solution obtained was filtered with a pinch of sodium sulphate and increased to 5 ml with hexane, and then 1µl litre of the sample prepared was injected and analyzed. Retention times of the selected pesticides are shown in Table 2.

Table 2. The retention times obtained for the organochlorine pesticides and recovery rates of these pesticides (six measurements)

Pesticides	Retention Time (min)	Detection Limit (µg/l)	Recovery Rate (%)±SD
α-HCH	10.98	0.010	91.92±7.3
β-HCH	12.01	0.020	92.55±7.6
γ -HCH	12.31	0.020	94.56±8.2
δ-HCH	13.27	0.008	91.99±9.1
Heptachlor	15.48	0.012	105.36±9.2
Aldrin	17.18	0.008	89.82±7.8
Heptachlor epoxide	19.27	0.020	87.05±8.3
α-Endosulfan	19.62	0.012	91.61±7.1
4,4'-DDE	21.76	0.008	90.51±9.5
Dieldrin	23.12	0.008	91.83±8.6
Endrin	23.81	0.012	106.89±8.3
β-Endosulfan	24.11	0.012	91.75±7.7
4,4'-DDD	24.44	0.008	91.36±7.3
Endrin aldehyde	24.66	0.012	87.76±8.2
Endosulfan sulfate	25.28	0.020	101.37±9.1
4,4'-DDT	25.91	0.012	86.95±7.1
Endrin Ketone	26.25	0.020	88.16±7.9
Methoxychlor	26.62	0.012	83.45±7.6

A florisil column system was used to remove the other pollutants from the extract. Diethyl ether and petrol ether were employed in order to elute the pesticides from the column (Shyre et al. 1998)

The analytical quality-control scheme included the periodic analyses of the organochlorine pesticides, standard mixtures, and the ultra pure water along with the samples. Using standard samples containing known amounts of pesticides, accuracy of the findings were routinely checked.

The recovery rates of the pesticides studied during the processing should be in between 80%-120% (Scieber 1999). Our recovery ratios are given in Table 2.

RESULTS

It is well known that most of the applied pesticides are subject to many transport and conversion products (Kalajzic et al. 1998, Soyöz and Özçelik 2003). Thus, they do not remain at their target site but often enter the aquatic environment via soil percolation, air drift or surface runoff, affecting abundance and diversity of non-target species, producing complex effects on the ecosystems, and altering tropic interactions (Mwevura et al. 2002,

Table 3. The concentrations of organochlorine pesticides detected in the drinking water samples from Afyonkarahisar province.

Organochlorine pesticides	Concentrations (min-max µg/l) Mean											
	1(N:6)	2(N:6)	3(N:6)	4(N:6)	5(N:6)	6(N:6)	7 (N:6)	8 (N:6)	9(N:6)	10(N:6)	11(N:6)	12(N:6)
α-HCH	ND-0.033 0.014	ND	ND	ND-0.038 0.019	ND	ND	ND-0.027 0.014	0.034-0.091 0.028	ND-0.056 0.013	ND-0.058 0.018	ND	ND-0.168 0.045
β-HCH	ND-0.155 0.035	ND-0.388 0.146	ND-0.544 0.239	ND-0.644 0.229	ND-0.617 0.281	ND-0.489 0.252	ND-0.196 0.078	ND-0.236 0.153	ND-0.353 0.124	ND-0.325 0.119	ND-0.208 0.092	ND-0.276 0.142
γ -HCH	ND-0.062 0.033	ND	ND	ND-0.033 0.026	ND	ND	ND	ND-0.107 0.028	ND-0.425 0.085	ND-0.089 0.031	ND	ND-0.243 0.051
δ-HCH	ND-0.060 0.014	ND-0.020 0.009	ND-0.053 0.019	0.008-0.032 0.012	ND-0.036 0.013	ND-0.028 0.008	ND-0.057 0.025	ND-0.088 0.042	ND-0.068 0.028	ND	0.009-0.123 0.044	ND-0.042 0.014
Heptachlor	ND-0.176 0.069	ND-0.202 0.062	ND-0.152 0.041	ND-0.069 0.033	ND-0.056 0.024	ND-0.029 0.011	ND-0.043 0.030	0.013-0.189 0.064	ND-0.130 0.054	ND-0.036 0.027	ND-0.116 0.051	ND-0.073 0.021
Aldrin	ND-0.016 0.009	ND	ND-0.043 0.024	ND-0.086 0.024	ND-0.048 0.024	ND-0.029 0.017	ND-0.296 0.056	ND-0.032 0.009	ND-0.086 0.020	ND	ND-0.055 0.028	ND
Heptachlor epoxide	ND	ND	ND	ND	ND	ND	ND-0.069 0.022	ND	ND-0.040 0.026	ND	ND	ND
α-Endosulfan	ND-0.056 0.018	ND	ND	ND-0.043 0.020	ND	ND	ND-0.060 0.020	0.013-0.052 0.021	ND-0.087 0.019	ND	ND 0	ND
4,4'-DDE	ND-0.108 0.032	ND	ND	0.009-0.038 0.017	0.010-0.030 0.015	ND	0.009-0.047 0.016	0.008-0.175 0.055	ND-0.046 0.015	ND	ND-0.049 0.026	ND-0.032 0.018
Dieldrin	ND	ND	ND	ND-0.136 0.036	ND 0	ND	ND 0	ND-0.030 0.012	0.012-0.067 0.023	ND	ND	ND-0.100 0.026
Endrin	ND-0.039 0.017	ND	ND	0.015-0.030 0.021	0.013-0.029 0.016	ND	0.013-0.055 0.018	0.012-0.252 0.075	ND-0.049 0.017	ND	ND	ND-0.030 0.015
β-Endosulfan	ND	ND	ND	ND	ND	ND	ND	ND-0.286 0.069	ND-0.156 0.037	ND	ND	ND
4,4'-DDD	0.010-0.068 0.017	ND-0.029 0.013	0.009-0.041 0.021	0.008-0.038 0.024	0.009-0.035 0.012	ND-0.035 0.019	ND-0.057 0.037	0.009-0.072 0.019	ND-0.084 0.034	0.011-0.201 0.057	0.012-0.049 0.028	0.009-0.161 0.044
Endrin aldehyde	ND-0.026 0.022	ND-0.044 0.024	ND-0.040 0.020	ND-0.023 0.018	ND-0.024 0.018	ND-0.055 0.020	ND-0.087 0.024	ND-0.118 0.054	0.013-0.037 0.015	ND-0.083 0.023	ND-0.099 0.033	ND-0.092 0.041
Endosulfan sulfate	ND-0.209 0.053	ND-0.049 0.025	ND-0.047 0.021	ND-0.043 0.021	ND-0.033 0.022	ND-0.040 0.022	ND-0.030 0.021	ND-0.036 0.022	ND-0.035 0.020	ND-0.078 0.031	ND-0.034 0.020	ND-0.040 0.026
4,4'-DDT	0.013-0.067 0.033	ND-0.326 0.120	ND-0.241 0.096	ND-0.173 0.092	ND-0.088 0.053	ND-0.066 0.029	ND-0.181 0.074	ND-0.118 0.051	ND-0.112 0.058	ND-0.455 0.099	ND-0.138 0.075	ND-0.115 0.046
Endrin Ketone	0.022-0.714 0.138	ND-0.066 0.024	ND	ND-0.083 0.024	ND-0.118 0.052	ND-0.049 0.021	ND	ND-0.040 0.028	ND	ND-0.095 0.024	ND	ND
Methoxychlor	ND	ND-0.063 0.024	ND-0.084 0.033	ND-0.154 0.032	ND-0.032 0.015	ND-0.042 0.018	ND	ND-0.094 0.035	ND-0.121 0.052	ND	ND-0.235 0.089	0.009-0.242 0.102

Sampling locations: 1- Çobanlar Advancement centre, 2- Çobanlar 7th Well , 3- Çobanlar 11th well, 4- Beşler Advancement center, 5- Beşler 7th well, 6- Bayraktepe well 7- Ali İhsanpaşa district, 8- Cumhuriyet district, 9- Karşıyaka district, 10- ANS Campus, 11- Karamık drinking water, 12-Bolvadin drinking water ND: not detected.

Table 4. The statistical analyses results of the data obtained from the 3 groups, Advancement centers (2 sampling sites), Main water supplying wells (4 sampling sites), and Water mains (6 sampling sites). * indicates the significance at $p<0.05$.

Pesticides	Advancement centers Concentrations (Mean±SD, µg/l)	Main water supplying wells Concentrations (Mean±SD, µg/l)	Watermains Concentrations (Mean±SD, µg/l)
α-HCH	0.022±0.043	0.004±0.004	0.017±0.032
β-HCH	0.131±0.181	0.229*±0.184	0.117±0.099
γ -HCH	0.010±0.018	0.000±0.002	0.033±0.081
δ-HCH	0.045±0.056	0.011±0.015	0.047±0.108
Heptachlor	0.019±0.023	0.034±0.054	0.041±0.045
Aldrin	0.016±0.024	0.016±0.016	0.029±0.053
Heptachlor epoxide	0.010±0.018	0.005±0.009	0.007±0.016
α-Endosulfan	0.021*±0.032	0.001±0.003	0.007±0.018
4,4'-DDE	0.010±0.015	0.008±0.010	0.021±0.034
Dieldrin	0.020±0.039	0.006±0.012	0.007±0.019
Endrin	0.004±0.008	0.005±0.007	0.020±0.050
β-Endosulfan	0.009±0.019	0.001±0.002	0.018±0.057
4,4'-DDD	0.023±0.010	0.015±0.014	0.036*±0.043
Endrin aldehyde	0.031±0.057	0.018±0.014	0.031±0.033
Endosulfan sulfate	0.026±0.021	0.021±0.015	0.018±0.016
4,4'-DDT	0.115±0.196	0.074±0.079	0.066±0.081
Endrin Ketone	0.020±0.023	0.026±0.029	0.013±0.018
Methoxychlorine	0.024±0.042	0.021±0.023	0.051*±0.066

In some cases ± SD values were found to be higher than that of the mean values. It was due to zero values (not detected) obtained from some specimens of the studied sampling sites. Similar findings were reported by Caldas et al. (1999), Mwevura et al. (2002), and Zhou et al. (2006)

Sankararamakrishan et al. 2005, Concha-Grana et al., 2006). Organochlorine pesticides have long lasting component and in nature, due to their molecular features and as a result of this, they accumulate and could reach a toxic dose for living things (Ahmed et al. 1998, Nasir et al. 1998, Konstantinou et al. 2005).

This study was conducted to determine the organochlorine pesticide residues in the drinking waters from six stations, 4 wells and 2 advancement centers, in Afyonkarahisar between June 2006 and April 2007. Water samples were collected biannually from the stations, and 18 different organochlorine pesticide derivatives were found. Results of the analysis of the water samples are summarized in Table 3. The statistical analysis results are shown in Table 4.

In accordance with the European Economic Commission (Anonymous 1980) for drinking water, the total pesticide level should not exceed 0.5 µg/l and an individual pesticide not greater than 0.1 µg/l. It was determined that the concentrations of organochlorine residues in some drinking water specimens were higher than that of the EC drinking water quality standards.

Only ß-HCH, 4,4'-DDT, endrin ketone, and methoxychlor's average concentrations were found to be at the higher level of acceptable limits. The highest pesticide concentration belonged to ß-HCH with a level of 0.281 µg/l. In the drinking water, aldrin, δ-HCH, α-HCH, endosulfan sulfate, heptachlor epoxide and α-endosulfan levels were found in trace amounts.

Fourteen different organochlorine pesticides were found in station 1. In this station the highest average level belonged to endrin ketone (0.138 µg/l) and the lowest was aldrin (0.009 µg/l). The first one had a much higher level in the dry season. In station 2 and 3, nine organochlorine pesticides were found. While ß-HCH had the highest value (0.146 µg/l), the peak level was in the dry season and δ-HCH having the lowest level (0.009 µg/l) in both stations. In station 4 sixteen different pesticides were seen. In this station again ß-HCH and δ-HCH were the highest and lowest levels (0.229 µg/l, 0.012 µg/l), respectively. Twelve pesticides were found in station 5. ß-HCH had the highest level with 0.281 µg/l and δ-HCH the lowest one with 0.013 µg/l. Ten organochlorine pesticides were found in station 6 and the highest and lowest were similar to stations 1-5, ß-HCH, 0.252 µg/l, and δ-HCH 0.008 µg/l, respectively. In station seven, thirteen different pesticides were found. Their highest and lowest levels were as follows: 0.078 µg/l ß-HCH and 0.014 µg/l α-HCH. As seen, α-HCH was replaced with δ-HCH. Seventeen different pesticides were detected in station eight. Aldrin was the lowest in this station. The highest and lowest pesticide concentrations were, ß-HCH (0.153 µg/l)

and aldrin (0.009 μg/l), respectively. In station nine, ß-HCH and α-HCH were the highest and the lowest level, 0.124 μg/l, and 0.013 μg/l, respectively. Nine pesticide residues were detected in the station ten. The highest and lowest levels belonged to ß-HCH (0.119 μg/l) and α-HCH (0.018 μg/l). Ten different pesticides were detected in station eleven. The highest and lowest levels were ß-HCH, and endosulfan with concentrations of 0.092 and 0.020 μg/l, respectively. Thirteen different pesticides were found in station twelve. The highest and lowest level being ß-HCH, and δ-HCH with concentrations of 0.142 and 0.014 μg/l, respectively. The highest concentration level belonged to ß-HCH in all stations examined except station 1.

DISCUSSION

As seen from the results, HCH isomers, DDT metabolites (especially 4,4'-DDT), endrin ketone and methoxychlor's average concentrations were found to be in higher levels than those of the EC's acceptable levels in Afyonkarahisar's waters in some seasons. It is interesting that their usage was banned a couple of decades ago. This could be because of their common usage in agriculture and forestry between 1940-1960. Their chemical features such as long lasting stability, high lipid, and low water solubility could have highly affected in their detection (Vural 1996). Moreover, their detection could be because of transportation by inner water from neighboring states. On the other hand, the main reason for Organochlorine pesticides contamination can be related to the still widely and illegal usage of Organochlorine pesticides in agriculture. Although use of 18 Organochlorine pesticides has been prohibited in Turkey by a decision made by the Turkish government in the 1980s, we observed that unfortunately illegal use of some Organochlorine pesticides continues in the agricultural areas.

Others, α-HCH, γ-HCH, δ-HCH and DDT metabolites such as 4,4-DDE' and 4,4'-DDD were detected in some stations and their concentrations were both in the acceptable limits of the EC regulations. Endosulfan sulfate, α-endosulfan, and ß-endosulfan were found in trace concentrations. Aldrin, dieldrin, endrin, heptachlor, and heptachlor epoxide were also detected in low concentrations.

The important harmful effects of these pesticides occur in aquatic systems. They can accumulate in water and then show their toxic effects. This effect causes the decrease of usable waters and has a bad effect on aquatic organisms directly. Because of these effects, water sources should be monitored continuously.

Irani et al. (2002) investigated 15 OCP residues in drinking waters around Delhi. They found that organochlorine pesticides in the ground water and irrigation water samples were below the Maximum Contaminant Level as prescribed by the WHO, and no organochlorine insecticides were detected in any of the drinking water samples.

El-Kabbany et al. (2000) investigated the pesticide levels in some water sources of the El-Haram, Giza. The water samples were collected from the El-Haram Giza canal water supplies in addition to the El-Moheet drainage water. They reported that residues of pesticides was varied and organochlorine pesticide residues in El-Moheet drainage water were relatively higher than in the canal water. They detected sixteen organochlorine pesticides in most of the water samples and their presence frequency, and order was as follow; drins (aldrin, endrin, dieldrin etc.)>total BHC>total DDT>endosulfan>heptachlor epoxide >heptachlor.

Turgut (2003) investigated the organochlorine pesticide and heavy metal contaminations in The Küçük Menderes River of Turkey. He reported that the contamination have remained although these pesticides were banned. He also reported DDT derivatives such as 4,4'-DDD in high concentration. The highest concentration belonged to heptachlor epoxide (281 ng/l).

Aydın and Yurdun (1999) reported the presence of α-HCH, γ-HCH and aldrin in the Istanbul waters. Their levels were under the acceptable limit values. Our findings showed that these pesticides are under the acceptable limits of the EC in Afyonkarahisar.

Zhulidov et al. investigated the presence of DDTs (DDT, DDE, DDD), and HCHs (α-HCH,γ-HCH) in the water, sediments and fish of north Russia. They found that 4,4'-DDT and 4,4'-DDE levels were higher than the acceptable limits and 4,4'-DDD was to be in the lower level of acceptable limits in the water. They reported the presence of α- HCH and γ-HCH in river sediments. In the present study it was found that the 4,4'-DDT level was over the acceptable limit while the 4,4'-DDD was lower (Zhulidov et al. 2002).

In our study, the statistical analysis results of the OCP levels of the advancement centers, main water supplying wells, and water mains were compared by

using a One Way ANOVA, Tukey, and Tamhone tests and $p<0.05$ was accepted as a significant sitatistical value (Table 4). As seen in Table 4, ß-HCH, α-endosulfan, 4,4'-DDD, and methoxychlorine levels differed significantly in all groups. In this table, some ± SD values were found to be higher than that of the mean values. It was due to zero values (not detected) obtained from some specimens of the studied sampling sites. Similar findings are in agreement with the findings of Caldas et al. (1999), Mwevura et al. (2002), and Zhou et al. (2006).

ß-HCH was found to be significantly high in the main water supplying wells, 4,4'-DDD, and Methoxychlorine levels were significantly high in the water mains when compared to the other sites. This could be due to unknown and unstudied wells in the study area. -Endosulfan levels were also significantly high in the advancement centers as compared to other sites. This could be because of the dilution of the water when it is mixed with the other sites' waters.

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REFERENCES

Ahmed MT, Saad MM, Mabrouk SS (1998) Residues of some chlorinated hydrocarbon pesticides in rain water, soil, and ground water, and their influence on some soil microorganisms. Environment International 24, 665-670.

Anonymous (1980) Official Journal of European Communities, EEC Council Directive 80/778/EEC Aug.30th, 229,11.

Anonymous (1989) Determination of chlorinated pesticides in water by gas chromatography with an electron capture detector. USEPA, Metod 508. National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OHIO, 45268.

Atamanalp M, Yanık T (2001) Pestisitlerin Cyprinidae'lere toksik etkileri. Ege Üniversitesi Su Ürünleri Dergisi 18, 555-563.

Ayas Z, Barlas N (1997) Determination of organochlorine pesticide residues in various environments and organisms in Göksu Delta, Turkey. Aquatic Toxicology 39, 171-181.

Aydın A., Yurdun T (1999) Residues of organochlorine pesticides sources of İstanbul. Water, Air and Soil Pollution 111, 385-398.

Caldas ED, Coelho R, Souza LCKR, Siba SC. (1999) Organochlorine pesticides in water, sediment, and fish of Paranoá Lake of Brasilia, Brazil. Bull. Environ. Contam. Toxicol. 62, 199-206.

Cerrillo I., Granada A, Lopez-Espinoza MJ, Olmos B, Jimenez M, Cano A, Olea N, Olea-Serrano MF (2005) Endosulfan and its metabolites in fertile women, placenta, cord blood, and human milk. Environmental Research 98, 233-239.

Concha-Grana E, Turnes-Carou MI, Muniategui-Lorenzo S, Lopez-Mahia, Prada-Rodrıguez D, Fernandez E (2006). Evaluation of HCH isomers and metabolites in soils, leachates, river water and sediments of a highly contaminated area. Chemosmphere 64, 588-595.

El-Kabbany S, Rashed MM, Zayed MA (2000) Monitoring of the pesticide levels in some water supplies and agricultural land, in El-Haram, Giza (A.R.E.). Journal of Hazardous Material 72, 11-21.

Golfinopoulos SK, Nikolaou AD, Kostopoulou MN, Xilourgidis NK, Vagi MC, Lekkas DT (2003) Organochlorine pesticides in the surface waters of Northern Greece. Chemosphere 50, 507-516.

Hernandez-Romero A, Tovilla-Hernandez C, Malo EA, Bello-Mendoza R (2004) Water quality and presence of pesticides in a tropical coastal wetland in southern Mexico. Marine Pollution Bulletin 48, 1130-1141.

Hung DQ, Thiemann W (2002) Contamination by selected chlorinated pesticides in surface waters in Hanoi, Vietnam. Chemosphere 47, 357 -367.

Irani M, Madhuban G (2002) Organochlorine insecticide residues in drinking and ground water in and around Delhi. Environmental Monitoring and Assessment 76, 93-185.

Kalajzic T, Bianchi M, Kettrup A (1998) Polychlorinated biphenyls (PCBs) and organochlorine pesticides in the sediments of an Italian drinking water reservoır. Chemosphere 36, 1615-1625.

Konstantinou I K, Hela D G, Albanis T A (2005) The status of pesticide pollution in surface waters(rivers and lakes) of Greece. Part I. Review on occurence and levels. Environmental Pollution 20, 1-16.

Manirakiza P, Covaci A, Nizigiymana L, Ntakimazi G, Schepens P (2002) Persistent chlorinated pesticides and polychlorinated biphenyls in selected fish species from Lake Tanganyika, Burundi, Africa. Environmental Pollution 117, 447-455.

Martinez MP, Angula R, Poza R, Jodral M (1997) Organochlorine pesticides in pasteurized milk and associated health risks. Food and Chemical Toxicology 35, 621-624.

Mwevura H, Othman CO, Mhehe GL (2002) Organochlorine pesticide residues in sediments and biota from the coastal area of Dar es Salam City, Tanzania. Marine Pollution Bulletin 45, 262-267.

Nasir K, Bilto YY, Al-Shuraiki Y (1998) Residues of chlorinated hydrocarbon insecticides in human milk of Jordanian women. Environmental Pollution 99, 141-148.

Rajendran RB, Imagawa T, Tao H, Ramesh R (2005) Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India. Environment International 31, 503-512.

Rovedatti MG, Castane PM, Topalian ML, Salibian A (2001) Monitoring of organochlorine and organophosphorus pesticides in the water of the Reconquista River. Water Research 35, 3457-3461.

Sankararamakrishnan N, Sharma AK, Sanghi R (2005) Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Utar Pradesh, India. Environment International 31, 113-120.

Seiber JN (1999) Pesticide residues in foods: convantional pesticide analytical methods. Wiley-Interscience Publication, New York.

Shukla G, Kumar A, Bhanti M, Joseph PE, Taneja A (2006) Organochlorine pesticide contamination of ground water in the city of Hyderabad. Environment International 32, 244-247.

Shyre M, Hanschmann G, Heber R (1998) Clean up procedure for monitoring chlorinated compounds in feed and crops. Journal of Association of Official Analytical Chemists 81, 513-517.

Soyöz M, Özçelik N (2003) Zirai mücadelede kullanılan pestisitlerin sitogenetik etkileri. Süleyman Demirel Üniveristesi Tıp Fakültesi Dergisi 10, 6-9.

Tieyu W, Yonglong L, Hong Z, Yajuan S (2005) Contamination of persistent organic pollutants (POPs) and relevant management in China. Environment International 31, 813-821.

Tsipi D, Hiskia, A (1996) Organochlorine pesticides and triazines in the drinking water of Athens. Bulletin Environment Contamination Toxicology 57, 250-257.

Turgut C (2003) The contamination with organochlorine pesticides and heavy metals in surface water in Küçük Menderes River in Turkey. Environment International 29, 29- 32.

Vural N (1996) Toksikoloji. Ankara Üniversitesi Eczacılık Fakültesi Yayınları 73, Ankara.

Zhou R, Zhu L, Yang K, Chen Y (2006) Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. Journal of Hazardous Materials 137, 68-75

Zuhulidov AV, Robarts RD, Headley JV, Liber K, Zhulidov DA, Zhulidova O V, Pavlov D F (2002) Levels of DDT and hexachlorocyclohexane in burbot (Lota lota) from Russian Arctic rivers. The Science of the Total Environment 292, 231-246.

Zulin Z, Huasheng H, Xinhong W, Jianqing L, Weiqi C, Li X (2002) Determination and load of organophosphorus and organochlorine pesticides at water from Jiulong River Estuary, China. Marine Pollution Bulletin 45, 397-402.