Bull. Environ. Contam. Toxicol. (2002) 69:236–242

DOI: 10.1007/s00128-002-0052-3

Bulletin of Environmental Contamination and Toxicology

Determination of Organochlorine Pesticide Residues in Water and Sediment Samples in Inner Anatolia in Turkey

N. E. Barlas

Hacettepe University, Science Faculty, Department of Biology, 06532, Beytepe, Turkey

Received: 10 October 2001/Accepted: 4 March 2002

Synthetic organic pesticides have been in widespread use for more than 40 years, and during that period, their use has contributed greatly to the increase in world-wide food production and at the same time improved human and animal health. However, these successes brought their side effects such as toxicities to non-target species, including humans, and the production of persistent residues in soil and water. That's why, some of them were commercially banned, but many are still in use because of their efficiency (e.g. lindane, endosulfan) and some or through their illegal entry in the country. Since they are intrinsically biocidal they are particularly dangerous when they enters water flux in significant quantities. Aquatic ecosystems may be contaminated by organochlorine insecticides used in crop protection. Pesticides are introduced into water systems from various sources such as industrial effluents, agricultural runoff and chemical spills. Even if these compounds are present only in very low concentrations in the water, they are hazardous because some species of aquatic life are known to concentrate them 1000-fold or more (Murty 1985). Unfortunately, these chemicals are not always selective and many have adverse effects on nontarget species. Organochlorine pesticides with their primarily hydrophobic chemical properties, occur as contaminants in estuarine systems partitioned between water and living and/or dead materials, with greatest affinity for the solid phase (Train 1979; Duursma et al. 1986). These compounds may also be detrimental to fish by interfering with their metabolism and/or reduce egg hatchability. Also, entry of these pesticides into the aquatic ecosystems will adversely affect many non target organisms including fish and birds (Ohlendorf et al. 1978a; Dutta et al. 1993; Ayas et al. 1997; Barlas 1999). Effects of DDE include egg shell thinning, egg breakage, and reduced clutch size, hatching success and subsequent productivity (Ohlendorf and Marois 1990).

In the present study, water and sediment samples collected from the Inner Anatolia lakes were analysed for the presence of some organochlorine pesticide residues and their metabolites to determine present contamination levels and accumulation pattern.

MATERIALS AND METHODS

The following wetlands were studied: Hirfanlı Dam Lake: 39° 10' N, 33° 39 E; Tuz Lake: 38° 45'N, 33° 22'E: Eşmekaya Marsches: 38° 15'N, 33° 28'E:

Tersakan Lake: 39° 05'N, 33° 50'E; Samsam Lake: 39° 06'N, 32° 45'E; Çöl Lake: 39° 18'N, 32° 54'E; Uyuz Lake: 39° 15'N, 32° 57'E.

Water and sediment samples were collected in three month intervals between April 1998 October 1999. These samples were collected 0.5 m below the water surface in 1 L pre cleaned glass bottles and were kept at -18 °C. The upper 10 cm of sediments were collected with Ekman sampler in a sterile 250 mL glass bottles. Organochlorine extraction of water samples was carried out according to Zweig method (1972). In this method, 900-950 mL water sample filtered before analyses than it was extracted with 25 mL n-hexane into a 1 L separate funnel three times. The combined extracts were dried over anhydrous sodium sulphate (0.5g). The extracts were evaporated at 50 °C until 1-2 mL left for the determination of organochlorines in water samples. Sediment samples were extracted with n-hexane using Soxhlet equipment for 4 hours (Sodergen and Wartiovaara 1988). Mixture standards of organochlorine pesticides were used for identification and measurements in GC. The extract was cleaned on a partially deactivated Flurosil column (FAO 1983). Organochlorine pesticides and metabolites (including op'-DDT, pp'-DDT, pp'-DDE, pp'-DDD, op'-DDD, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, lindane, α-BHC and β-BHC) were analysed with a Chrompac-SFC Instrument 138 A with a Nickel Electron Capture detector automatic sampler, digital processor and 4% SSE- 30/60 % QF-capillary column. The column temperatures were programmed at 270 °C. Nitrogen at a flow rate of 40 mL/min was used as a carrier gas. Duplicate injections (0.8 μL) of each sample were analysed.
All residues are expressed as μg /g. Minimum, maximum and geometric means were used to express residue levels. According to this method, the detection limit is 0.0001μg /g. Values below detection limits were assigned as a Not-Detectable (ND).

A student's *t*-test was used to determine differences in some organochlorine pesticide residues in water and sediment samples (Sümbüllüoğlu and Sümbüllüoğlu 1987). The 0.05 level of significance for probability was used as the criterion of statistical significance.

RESULT AND DISCUSSION

Prior to the restriction or ban on the use of many organochlorine pesticides, residues of the more commonly used compounds were detected in natural freshwater bodies. A total of 13 organochlorine pesticide and their residues have been determined. Organochlorine residues in water and sediment samples are shown in Table 1 and Table 2.

In these tables OC pesticide residues in sediment samples were generally higher than residue levels in water samples. Alpha BHC, beta-BHC, heptachlor epoxide, aldrin, op'-DDT, op' DDD, pp'-DDT were detected at high levels in sediment samples. In Tuz Lake, Hirfanlı Dam Lake, Eşmekaya Lake, Tersakan Lake, Kozanlı Lake and Kulu Lake, organochlorine pesticide residues (especially alpha-

BHC, beta-BHC, aldrin, dieldrin, heptachlor epoxide, and DDT metabolites op'-DDD, pp'-DDT, pp'-DDD) in water and sediment samples were generally higher than in other lakes, because they are located in wide agricultural areas.
The highest average amount of extractable alpha-BHC was 1.38 μg/g (range ND-2.719 μg/g mean) which was found in the sediment sample of Bolluk lake. The highest residue levels of heptachlor epoxide was 1.394 μg/g which was found in sediment samples of Kozanlı Lake. Also, the highest average amount of extractable beta-BHC (2.328 μg/g mean of Hirfanlı Dam Lake) and lindane (1.79 μg/g mean in Tuz Lake) were detected in sediment samples. DDT and it's metabolites pp'-DDE, op'-DDD, op'-DDT, pp'-DDD, pp'-DDT (mean concentrations 1.421, 1.389, 2.244, 0.969, 1.152 μg/g in Tuz Lake, Hirfanlı Dam Lake, Tuz Lake, Tuz Lake and Samsam, respectively) were detected at high levels in sediment samples. This high residue levels of pesticides may be due to continuous usage of organochlorine pesticides.

On the other hand, Fay and Newland reported that no such relationship existed between the insecticides present in water and those in the sediments. These researchers concluded that heptachlor, endrin, and pp'-DDT were detected higher in water whereas dieldrin and pp'-DDD were detected in sediments (Fay and Newland 1972).

In this study, it was established that aldrin had higher concentration than it's converted products in sediment samples in Hirfanlı Dam Lake and Eşmekaya Lake. Normally, aldrin is converted to its epoxide analogue dieldrin, heptachlor is metabolised to heptachlor epoxide, isodrin is metabolically converted to endrin by mammals, soil microorganisms, plants and insects (Matsumura 1985). Unfortunately, the residue level of aldrin, dieldrin and some DDT metabolites seem to be in very unusual proportions. These results may be due to still using OC pesticides and other environmental factors such as soil types, P^H , temperature in the study area. In Tuz Lake, op'- DDT was found in greater concentrations than pp'-DDE in sediment samples, but, in same lakes DDE was found at higher degrees than DDD. Many authors have concluded that pp'- DDE was detected to a higher degree than DDT in soil, sea bird tissue and their eggs (Fasola et al. 1987; Hernandez et al. 1988). Also, some researchers have concluded that DDT, aldrin and heptachlor have been found in higher quantities than their converted products (Ayas et al. 1997; Barlas 1999). Although the usual route of metabolism of DDT in insects and in other organisms and in sediments appears to be through DDE. pp-DDE is the terminal product of pp-DDT. DDT was used extremely effectively in control of some pest disease, but DDT is dangers of indiscriminate usage of substances. The sheer fact that DDT was a persistent chemical in the environment, it did not degrade rapidly. Also, DDT was an added factor in the chain of events which led us to realise that use of such compounds need to be strictly controlled, and that effectiveness over long periods alone is not a formula for the continuous health of the environment (Connell et al. 1999). Ayas et al. found that OC levels were highest at the top of the food chain in Göksu Delta in Turkey. Göksu Delta is an important wetland, because a lot of rare and endangered water-birds which are in the food chain could be the most affected organisms and OC could affect

Table 1. Residue levels of organochlorine pesticides (μg/g) in water and sediment samples, collected from Inner Anatolia in Turkey, during 1999-2000.

	Tuz Lake		**Hirfanlı Dam Lake**		**Eşmekaya Lake**		**Tersakan Lake**		**Bolluk Lake**	
Organochlorine compounds	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10
Alpha-BHC	ND-1.069 0.525	ND-1.519 0.797	ND	ND	ND-1.036 0.345	0.652-2.13 1.246	ND	0.04-1.857 0.634	ND-0.785 0.246	ND-2.719 1.386
Beta-BHC	ND	ND-3.04 1.674	ND	ND-3.23 2.328	ND-0.688 0.229	0.397-3.97 1.678	ND	0.91-2.44 1.476	ND	1.148-3.87 1.958
Lindane	ND-0.163 0.02	ND-3.84 1.79	ND	ND	ND	2.311-3.156 2.586	ND	1.52-2.68 1.642	ND	ND
Aldrin	ND	ND-2.324 0.524	ND-0.148 0.123	ND-2.542 2.218	ND	0.765-4.426 2.298	ND	ND	ND	ND-1.589 1.459
Dieldrin	ND-1.17 0.562	ND-1.329 0.710	ND	ND	0.037-0.746 0.398	ND	ND-0.47 0.36	ND	ND-0.027 0.011	ND
Endrin	ND-0.403 0.188	ND-1.46 0.640	ND	ND-0.373 0.05	ND	0.203-0.662 0.451	ND	ND-0.559 0.366	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND-0.49 0.215	ND	0.94-1.25 1.031	ND	ND
Heptachlor epoxide	ND-0.273 0.25	ND-1.677 1.144	ND	ND-2.55 1.385	ND	0.362-0.993 0.617	ND	0.27-1.423 0.961	ND	ND-1.171 0.95
op'-DDT	ND	1.010-3.540 2.244	ND	ND	ND-0.415 0.284	ND-0.554 0.251	ND	ND	ND-0.312 0.026	ND
pp'-DDT	0.181-1.955 0.831	0.042-2.93 1.307	ND-0.224 0.098	ND-0.375 0.254	0.148-1.184 0.633	0.147-1.224 0.55	ND-0.425 0.226	ND-0.385 0.37	ND-0.198 0.08	ND-0.616 0.384
op'-DDD	ND-2.412 1.236	ND-1.798 0.527	ND-1.446 0.793	0.088-3.99 1.389	0.213-0.47 0.391	ND	ND-0.487 0.193	ND	ND	ND-0.06 0.007
pp'-DDD	0.301-1.169 0.682	0.153-2.66 0.969	ND-0.311 0.132	ND-0.567 0.296	ND-0.311 0.273	ND-0.741 0.47	ND-0.402 0.29	ND-0.294 0.152	ND	ND-0.542 0.36
pp'-DDE	ND-0.429 0.283	ND-2.309 1.421	ND-0.784 0.212	ND-1.443 0.677	0.128-1.115 0.881	0.006-0.278 0.11	ND-0.35 0.265	ND	ND	ND

ND: Not Detectable.
n: number of samples

Table 2. Residue levels of organochlorine pesticides (μg/g) in water and sediment samples, collected from Inner Anatolia in Turkey, during 1999-2000.

	Kulu Lake		Kozanlı Lake		Samsam Lake		Çöl Lake		Uyuz Lake	
Organochlorine compounds	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10	Water (Min-Max) *n*: 10	Sediment (Min-Max) *n*: 10
Alpha-BHC	ND	ND-0.388 0.224	ND	ND-0.352 0.121	ND	ND-0.393 0.350	ND	ND	ND	ND
Beta-BHC	ND	ND-0.504 0.341	ND	ND-1.559 0.978	ND	ND-1.765 1.157	ND	ND-2.154 1.382	ND	ND-1.283 0.96
Lindane	ND	ND	ND	ND	ND	ND	ND	ND-1.779 1.03	ND	ND
Aldrin	ND	ND	ND-0.532 0.325	ND-2.145 1.286	ND	ND-2.09 1.453	ND	ND-1.135 0.781	ND	ND
Dieldrin	ND-1.303 0.751	ND	ND-0.725 0.392	0.236-2.547 1.376	ND	ND	ND	ND	0.183-0.235 0.216	ND-0.06 0.02
Endrin	ND-0.628 0.285	ND-1.094 0.864	ND-0.165 0.037	ND-0.192 0.09	ND	ND-0.47 0.356	ND-0.719 0.067	ND-0.745 0.345	ND-0.446 0.349	ND-0.871 0.66
Heptachlor	ND	ND	ND	ND	ND	ND-0.49 0.215	ND	1.09-2.34 1.126	ND	ND
Heptachlor epoxide	ND	ND	ND-1.179 0.758	ND-1.516 1.394	ND	ND-1.655 1.294	ND	ND-1.693 0.919	ND	0.22-1.48 1.035
op'-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND-0.5 0.324	ND
pp'-DDT	ND-0.415 0.303	ND-1.748 0.828	ND-1.588 1.039	ND-0.339 0.245	ND	ND-1.955 1.152	ND-0.458 0.254	ND	ND-0.79 0.53	ND-0.492 0.482
op'-DDD	ND-0.14 0.08	ND-0.494 1.115	ND-1.144 0.75	ND-0.475 0.118	ND-0.297 0.154	ND	ND	ND-1.032 0.826	ND-0.408 0.289	ND-0.35 0.266
pp'-DDD	ND	ND-0.293 0.147	ND	ND-0.305 0.156	ND-0.153 0.587	ND-1.764 0.967	ND	ND-0.417 0.311	ND-0.439 0.195	ND-0.718 0.599
pp'-DDE	ND	ND-0.397 0.282	ND	ND-1.492 0.76	ND	ND	ND	ND	ND-2.858 0.519	0.043-0.2 0.09

ND: Not Detectable.
n: number of samples

the reproductive success of these birds (Ayas et al. 1997). Barlas was found the same results in Sakarya basin in Turkey (Barlas 1999). Also, she concluded that, DDT metabolites were accumulated in fish adipose tissue and some pathological findings were seen in gill, liver and kidney tissue of fish (Barlas 1999).

In spite of use of all OC pesticides has been prohibited in Turkey by a decision made by the Turkish government in 1980s; a lot of organochlorine pesticides and their degradation products were detected at high levels in water and sediment samples. The main reason of high OC contamination can be related to the still widely and illegal use of OC pesticides in agriculture. Toxic substances which occur at such low concentrations in water at to pose no threat through direct toxicity, may, if absorbed, be accumulated in the food chains and affect aquatic organisms and their predators.

Acknowledgments. I thank Dr. Aydın Akbulut for collecting sediment and water samples. Also, this study was supported by the Ministry of the Environment (Çevre Koruma Genel Müdürlüğü, Hassas Ekosistemler ve Korunan Alanlar Dairesi Başkanlığı).

REFERENCES

Ayas Z, Barlas N, Kolankaya D (1997) Determination of organochlorine pesticide residues in various environments and organisms in Göksu Delta, Türkiye. Aquat Toxicol 39: 171-181

Barlas NE (1999) Determination of Organochlorine Pesticide Residues in Aquatic Systems and Organisms in Upper Sakarya Basin, Türkiye. Bull Environ Contam Toxicol 57: 705-712

Barlas NE (1999) Yukarı Sakarya Havzasında Yaşayan Sazan (*Cyprinus carpio*) Balıklarının Solungaç, Karaciğer ve Böbrek Dokularının Histopatolojik Olarak İncelenmesi. Turkish J Vet Anim Sci 23 : 277-284

Connell D, Lam P, Richardson Bb, Wu R (1999) Introduction to ecotoxicology. Blackwell Sciences Ltd. UK, p170

Duursma E K, Nieuwenhuyze, JVan Liere J M (1986) Partitioning of some organochlorines between water, particulate matter and some organisms in estuarine and marine systems of the Netherlands. J Sea Res 20: 239-251

Dutta HM, Richmonds CR, Zeno T (1993) Effects of diazinon on the gills of Bluegill sunfish *Lepomis macrochirus*. J Environ Path Toxicol Oncol 12 : 219-227

FAO (1983) Manuals of Methods in Aquatic Environment Research, Part 9. Analyses of metals and organochlorine pesticides in fish. Tech Pap No: 212, 34

Fasola M, Vecchio I, Coccialanza E, Gandini C, Kitsos M (1987) Trends of organochlorine residues in eggs of bird from Italy, 1977 to 1985. Environ Pollut 48: 25-36

Fay RR and Newland LW (1972) Organochlorine insecticide residues in water, sediment, and organisms. Aransas Bay, Texas-September 1969 - June 1970. Pesticide Monitoring 1 (6) : 97

Hernandez LM, Gonzalez MJ, Rico MC, Fernandez MA, Aranda A (1988) Organochlorine and heavy metal residues in falconiforme and ciconiforme eggs (Spain). Bull Environ Contam Toxicol 40: 86-93

Matsumura F (1985) Toxicology of insecticides. Second Edition Plenum press. New York. p410
Murty AS (1985) Toxicity of pesticides to fish Volume II, CRC Press, Inc p143
Ohlendorf HM, Risebrough RW, Vereer K. (1978a) Wildlife Research Report No:9, US: Fish and Wildlife Service, p40
Ohlendorf HM and Marois KC (1990) Organochlorines and selenium in california night-heron and egret eggs. Environ Monit Assess 15: 91-104
Sodergen A, Wartiovaara J (1988) Methods for determination of organochlorine compounds in water, sediment and biological samples. Water Sci Technol 20 (2):13-24
Sümbüllüoglu K, Sümbüllüoglu V (1987) Biyoistatistik Ankara p214
Train RE (1979) Quality criteria for water. US Environmental Protection Agency, Washington D C, Castle House Publications LTD p256
Zweig G (1972) Analytical methods for pesticides and plant growth regulators, Vol VI, Academic Press, New York