

## Organochlorine Contamination in Three Species of Diurnal Raptors in León, Spain

Matilde Sierra, <sup>1</sup> María Teresa Terán, <sup>1</sup> Ana Gallego, <sup>2</sup> María José Díez, <sup>3</sup> and Diego Santiago<sup>4</sup>

<sup>1</sup>Department of Biochemistry and Molecular Biology, Biology, Physiology and Pharmacology, Faculty of Veterinary, The University of León, 24071 León, Spain; <sup>2</sup>Titular Veterinary Municipal Slaughterhouse of Pontevedra, 36071 Pontevedra, Spain; <sup>3</sup>Department of Hygiene and Food Technology and Toxicology, Faculty of Veterinary, The University of León, 24071 León, Spain; and <sup>4</sup>Department of Pharmacology and Toxicology, Faculty of Veterinary, The University of Cordoba, 14071 Cordoba, Spain

The purpose of this paper is to give new data on the levels of organochlorine pesticides residues in birds of prey collected in the province of Leon, in the North-West of Spain.

This study was undertaken to determine organochlorine residual levels in tissues and organs (muscle, liver, kidney, fat and brain) of 9 diurnal raptors, including kestrel, Falco tinnunculus, L., sparrow hawk, Accipiter nisus, L. and red kite, Milvus milvus, L.

The use of organochlorine pesticides has been restricted because of their persistence in the environment and potential for environmental impact. Even with the restrictions on their use in this country, organochlorine pesticides residues are present in animal population in the province of Leon (Sierra et al., 1984, Sierra and Santiago, in press) due to their slow rate of degradation (Edmundson, 1972, Nash and Woolson, 1967).

## MATERIALS AND METHODS

A total of 35 samples of muscle, liver, kidney, brain and fat were obtained from 4 kestrels, 3 sparrow hawks and 2 red kites.

Portions of about 4 grams were taken from liver, muscle and kidney and the whole of the brain was removed for organochlorine residues analysis. The weight of perivisceral fat samples was variable depending on the body fat reserves. It was only possible to obtain 5 samples of fat (2 of them were from kestrels, 2 from sparrow hawks and 1 from red kites). All samples were frozen to -20°C until analyses could be conducted.

Each sample was individually homogenized (Ahmad, 1979). Subsequent extraction and clean-up were the same as those described by Richardson  $\underline{\text{et}}$   $\underline{\text{al.}}$ , 1971.

Send reprint requests to Matilde Sierra at the above address.

TABLE 1.- Average, range (in ppm/wet weight) and incidence percent of organochlorine pesticides in sparrow hawks.

	KIDNEY	LIVER	BRAIN	FAT	MUSCLE
	0.510	0.385	0.642	0.829	0.341
1	0.393-0.607	0.078-0.991	0.352-1.207	0.563-1.094	0.341
	100	100	100	100	100
	0.027	0.203	0.059	0.216	0.012
2	0.017-0.036	0.004-0.597	0.008-0.109	0.216	0.012
	66.67	100	66.67	50	100
	0.014	0.035	0.019	0.285	0.028
3	0.014	0.035	0.008-0.030	0.285	0.028
	33.33	33.33	66.67	100	100
	<del></del>			0.009	
4				0.009	
				50	
	0.400	0.139	0.031	1.068	0.047
5	0.400	0.007-0.270	0.031	0.174-1.961	0.047
	33.33	66.67	33.33	100	100
	0.445	0.364	0.130	17.338	<del></del>
6	0.445	0.364	0.042-0.21	7 17.338	
	33.33	33.33	66.67	50	
	0.541	<del></del>			
7	0.541				
	33.33				<del></del>
	1.922	0.368	0.035	4.543	9.969
8	1.415-2.429	0.150-0.492	0.012-0.057	3.896-5.189	9.969
	66.67	100	66.67	100	100
	5.152	7.543	3.388	48.588	7.381
9	1.842-9.099	1.147-18.62	0.177-9.028	31.14-66.03	7.381
	100	100	100	100	100
10	1.323	0.583	0.057	8.557	<del></del>
	0.234-2.412	0.036-1.129	0.022-0.091	6.469-10.64	<del></del>
	66.67	66.67	66.67	100	

<sup>1: \( \</sup>mathcal{L}\)-HCH; 2: Lindane; 3: Heptachlor-epoxide; 4: Aldrin; 5: Endrin 6: Dieldrin; 7: o,p'-TDE; 8: p,p'-TDE; 9: p,p'-DDE; 10: p,p'-DDT

TABLE 2.- Average, range (in ppm/wet weight) and incidence percent of organochlorine pesticides in red kites.

	KIDNEY	LIVER	BRAIN	FAT	MUSCLE
	0.010	0.020	0.450		
1	0.010	0.013-0.026	0.162-0.738		· · · · · · · · · · · · · · · · · · ·
	100	100	100		
2	0.006	0.007	0.011	0.437	0.005
	0.006	0.007	0.010-0.011	0.437	0.005
	100	50	100	100	100
	<del></del>		0.056		
3		-	0.034-0.078		
	<del>naturbay and Tan</del>	<del></del>	100	**************************************	V-1-12-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1
		<del></del>	0.014	~ <del></del>	
4	<del></del>		0.014	<del></del>	<del></del>
	<del></del>	-	50		
	0.005	W-1	0.103	2.035	
5	0.005	**************************************	0.103	2.035	
	100		50	100	
	0.155	0.099	0.017	0.197	0.013
6	0.155	0.077-0.120	0.016-0.018	0.197	0.013
	100	100	100	100	100
	0.020		0.077	0.124	·
7	0.020	*	0.025-0.129	0.124	·
	100	<del></del>	100	100	
	0.665	0.018	0.152	2.684	
8	0.665	0.018	0.025-0.279	2.684	
	100	50	100	100	
	0.028	0.875	0.056	-	0.208
9	0.028	0.112-1.638	0.018-0.093		0.208
	100	100	100	<del></del>	100
	2,496	0.160	1.610	0.762	0.063
10	2.496	0.160	1.610	0.762	0.063
	100	50	50	100	100

TABLE 3.- Average, range (in ppm/wet weight) and incidence percent of organochlorine pesticides in kestrels.

	KIDNEY	LIVER	BRAIN	FAT	MUSCLE
1	0.456 0.216-0.735 100	0.255 0.053~0.455 75	0.343 0.078-0.929 100	1.368 0.583-2.153 100	1.266 1.122-1.410 100
2		0.024 0.012-0.035 100	0.015 0.003-0.019 100		0.156 0.079-0.232 100
3	1.132 0.589-2.042 75	0.031 0.003-0.080 100	0.033 0.012-0.051 100	2.040 0.284-3.795 100	0.183 0.139-0.226 100
4	0.217 0.140-0.371 75	0.048 0.043-0.053 50	0.030 0.018-0.038 75	0.654 0.654 50	0.074 0.020-0.127 100
5 -	0.027 0.013-0.040 50	0.010 0.010 25	0.016 0.016 25		0.054 0.054 50
6		0.151 0.009-0.292 50	0.005 0.005 25		0.046 0.046 50
7	0.288 0.288 25			0.691 0.691 50	
8	0.028 0.028 25	0.006 0.006 25	0.012 0.012 25		
9	0.238 0.124-0.320 100	0.063 0.011-0.161 75	0.046 0.007-0.092 100	2.889 1.668-4.110 100	0.149 0.032-0.266 100
10	0.045 0.028-0.064 75	0.015 0.007-0.022 50	0.057 0.057 25	1.250 0.483-2.017 100	0.091 0.013-0.168 100

<sup>1: ≪-</sup>HCH; 2: Lindane; 3: Heptachlor-epoxide; 4: Aldrin; 5: Endrin 6: Dieldrin; 7: o,p'-TDE; 8: p,p'-TDE; 9: p,p'-DDE; 10: p,p'-DDT

A florisil column conditioned for 24 hours at 130°C was used to remove interfering substances and to separate the pesticides in two fractions.

The eluates were concentrated for analysis by electron capture gas chromatography, which was performed on a Hewllett Packard gas chromatograph fitted with a nickel 63 electron capture detector.

The chromatographic parameters were: 1.- Columns: (a) 6 feet long and 1/4 inch inside diameter, containing a 1.5% coating of OV-17/1.95% of QF-1 on 100-120 mesh chromsorb W (AW/DMCS) and (b) 3.8% of SE-30 on 80-100 mesh chromsorb W (AW/DMCS). 2.- Carrier gas: 5% argon-methane at a flow rate of 25 ml/min. 3.- Operating temperatures: Inlet, 250°C; Detector, 300°C; Column (a) 200°C and Column (b) 180°C.

In order to identify the pesticides and quantify the residual levels, we have compared the problem solutions with a standard solution containing the following pesticides:  $\not \sim$ -HCH, lindane, heptachlor-epoxide, aldrin, dieldrin, endrin, o,p'-TDE, p,p'-DDE and p,p'-DDT.

## RESULTS AND DISCUSSION

The incidence percent of organochlorine pesticides in the five types of samples and the mean residue levels and ranges (in parts per million, ppm, by weight of wet sample) are given in Tables 1 to 3.

Our results show that sparrow hawk is the most contaminated species.

√-HCH was present in all the samples of organs and tissues analyzed in these raptors. We have obtained identical results in earlier studies in buzzards (Sierra et al., 1984). The incidence percent detected for lindane, dieldrin and heptachlor-epoxide was similar to those reported by Joiris et al., 1979, in liver, stomach content and muscle samples: 80% for lindane, 60% for dieldrin and 50% for heptachlor-epoxide.

The mean residue levels of DDT and related compounds (o,p'-TDE, p,p'-TDE, p,p'-DDE and p,p'-DDT) detected in sparrow hawks were 8 times higher than those indicated by Joiris et al., 1979.

p,p'-DDE was detected at high concentrations in all the organs and tissues samples, specially in fat in which the average for this pesticide was 48.6 ppm. The accumulation of important levels of DDE in this species can be explained because birds are included in its diet.

However, the residual levels of p,p'-DDE detected in liver samples are lower than those reported by Newton et al., 1982. These authors found more than 100 ppm of p,p'-DDE in liver samples of sparrow hawks collected in England, U.K. The highest

concentration we have detected was 18.6 ppm. Juillard et al., 1978, detected 195 ppm of p,p'-DDE in liver samples from sparrow hawks collected in Laussanne (Switzerland), this concentration is more than 25 times higher than ours (7.5 ppm).

The red kite was the species least contaminated. The bibliographic references found about this species are limited. Joiris  $\underline{\text{et}}$   $\underline{\text{al.}}$ , 1974, detected in liver and muscle samples a burden of organochlorine pesticides of 0.63 ppm; this amount is similar to 0.69 ppm obtained by us averaging the residual levels detected in both types of samples. The mean residue levels of DDT and related compounds, 0.62 ppm, are higher than those reported by these authors, 0.26 ppm.

The residual levels detected in organs and tissues of red kite are not very high and this fact is probably due to diversified feeding.

Compared to the other two species, kestrels had intermediate mean residue levels.

Joiris et al., 1979 and Juillard et al., 1978, indicate organochlorine pesticide residual levels in this species higher than ours. Newton et al., 1982, found more than 100 ppm of p,p'-DDE and dieldrin in liver samples of kestrels collected in England, U.K. The higher concentrations we have detected were 0.29 ppm for dieldrin and 0.16 ppm for p,p'-DDE.

However, heptachlor-epoxide was detected in every sample of liver, brain, muscle and fat and in 75% of kidney samples. In a similar way, high incidence percent of this pesticide was also indicated by Lavaur de and Arnold, 1977, in several species of birds in France.

## REFERENCES

Ahmad N (1979) Cleanup of biological samples for determining p,p'-DDT and its metabolites. J Assn Offic Anal Chem 62: 1150-1154

Edmundson WF (1972) Pharmacology of DDT the background. In: Davies JE, Edmundson WF (eds) Epidemiology of DDT. Futura Publishing Co, Inc, Mount Kisco NI, 9-25

Joiris C (1974) La contamination par pesticides organochlorés des oiseaux de proie en Belgique. Semaine d'Etude Agriculture et environment, September, Grembloux, Belgique, 479-483

Joiris C, Delbeke K, Martens E, Lauwereys M, Vercruysse A (1979) PCB and organochlorine pesticides residues in birds of prey found dead in Belgium from 1973 to 1977. Gerf Gierv 69:319-337 Juillard M, Praz JC, Etournaud A, Beaud P (1978) Donnés sur la contamination des rapaces de Suisse Romande et de leurs œufs par les biocides organochlorés, les PCB et les métaux lourds.

Nos Oiseaux 34:189-206

Lavaur E de, Arnold A (1977) Pesticides et faune sauvage: resultats des analyses toxicologiques effectuées sur le gibier de 1974 a 1976. Phytiatrie-Phytopharmacie 26:159-168

Nash RG, Woolson CA (1967) Persistence of chlorinated hydrocarbon insecticides in soils. Science 157:224-227

Newton I, Bell AA, Wyllie I (1982) Mortality of sparrow hawks, Accipiter nisus, and kestrels, Falco tinnunculus. Br Birds 75:195-204

Richardson A, Robinson J, Crabtree AN, Baldwin MK (1971) Residues in fish, wildlife and stuaries. Pestic Monitor J 4:169-176
Sierra M, Gallego A, Terán T, Santiago D (1984) Niveles de resíduos de &-HCH, p,p'-DDE y p,p'-DDT en tejidos de ratonero común (Buteo buteo, L.) capturados en la provincia de León. Revista de Toxicología 1:67-73

Sierra M, Santiago D (in Press) Organochlorine pesticide levels in barn owls collected in Leon, Spain

Received May 16, 1986; accepted September 15, 1986