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Organochlorine Pesticide and PCB Residues in Wild Bird Eggs from the South-West of Spain

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The major low-level pollutant threats to wild birds resources that have been clearly demonstrated are the persistent pesticides, polychlorinated biphenyls (PCB's) and some heavy metals. It is well known that chlorinated hydrocarbons are implicated in the environment deterioration because of their incidence on the energetic flux of the ecosystems.

In a previous paper (BALUJA and HERNANDEZ, in press) results were reported on levels of organochlorine residues in muscle, liver, kidney, brain, and gonad in species of purple heron (Ardea purpurea) and spoon duck (Anas clypeata) collected in the Biological Reserve of Doñana (South-West of Spain). The purpose of this paper is to give new data on the levels of organochlorine pesticides and PCB residues in eggs of birds from the South-West of Spain, mainly the natural Reserve of Doñana, with the aim of finding if there exists some class of incidence of the organochlorine residues on the life of wildbirds living in that area whose populations appear to be declining lately.

MATERIALS AND METHODS

Eggs of fourteen different species were collected during the nesting season between 1972 and 1976. A total of 52 eggs were chosen at random, classified according to the distribution shown in Table 1, and analyzed individually for residues of organochlorine pesticides and PCB's after each collecting season.

All eggs were frozen after collection until preanalytical treatment was performed. This treatment basicaly consists in the homogenization of each egg content, extraction of homogenates, and clean-up according to the methods provided by ONLEY and MILLS (1962) and REYNOLDS (1969). All extracts were eluted through an activated florisil column to separate pesticides and PCB's in two fractions, and analysis were conducted by gas-liquid chromatography using

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an electron affinity detector following methods already described in previous papers (BALUJA et al., 1970, 1972).

TABLE I

Sites and bird species from which eggs were collected

Sites	Year	Eggs and species
Biological Reserve of Doñana	1972	1 Ardea purpurea (Purple heron); 1 Fulica atra (Coot); 3 Aythya ferina (Pochard)
	1973	4 Aythya ferina; 5 Aquila heliaca (Imperial eagle); 3 Anas clypeata (Spoon duck); 1 Recurvirrostra avoseta (Avocet); 2 Podiceps sp.; 7 Sterna sp. (Commun tern); 5 Glareola pratincola (Pratincole); 8 Sterna albifrons (Litle tern)
	1974	1 Aquila heliaca
	1975	1 Falco subbuteo (Lanner)
	1976	4 Milvus migrans (Black kite); 2 Aquila heliaca
Province of Salamanca	1975	1 Hieraetus pennatus (Booted eagle); 1 Otis tarda (Bustard)
Province of Cáceres	1976	2 Aquila heliaca

Extracts were analyzed for α-and γ-HCH, heptachlor, heptachlor-epoxide, aldrin, dieldrin, endrin, op-DDT, pp'-DDE, pp'-TDE, pp'-DDT and PCB's; PCB's were quantified using a standard of Aroclor 1260 whose peak pattern most closely resembled the pattern in the analytical sample. Average percentage recoveries ranged from 90 to 110 but residue data in the tables were not adjusted on the basis of these recoveries. Two columns were used whose operating parameters are given in Table 2.

Some residue identifications were confirmed by methods of chemical derivatization.

RESULTS AND DISCUSSION

The mean residue levels and ranges of organochlorine pesticides and PCB's are summarized in Tables 3 and 4

expressed in parts per million by weight of wet sample. The first observation of values permit the assumption that both classes of residue levels varied greatly among and within species but all exceeded trace values in most eggs, except that cyclodienic residues were not detected in eggs of pochard collected in the consecutive seasons of 1972-1973.

TABLE II

Columns and operating conditions

	Glass columns, 1.20 m length, 4 mm O.D.	
	A	B
Support and mesh size	Chromosorb W HP/ 80-100	Chromosorb W HP/ 80-100
Liquid phase	5% DC-200/7.5% QF-1	2% Oronite polybutene 128/1.95% QF-1
Gas flow rate N_2	40 ml/min.	55 ml/min.
Column temp.	190º C	170º C
Detector temp.	210º C	190º C
Sensitivity	0.001 ppm dieldrin	0.001 ppm dieldrin

Aldrin, dieldrin, op-DDT, heptachlor, and heptachlor-epoxide were detected as trace amounts in most eggs collected in 1972 and 1973, but heptachlor-epoxide and dieldrin occurred more frequently in eggs collected in 1975 and 1976 at levels ranged from 0.001 ppm to 0.426 ppm; the highest levels were found in eagle eggs. DDE, TDE, and DDT were always easily detected in all eggs. DDE ranged from 0.100 ppm to 9.202 ppm and total DDT-group ranged from 0.157 ppm to 9.917 ppm; the highest levels were found in black kite and imperial eagle eggs sampled in 1976. Higher PCB residues were found in imperial eagle eggs with a range between 0.599 ppm and 7.742 ppm, but the highest PCB level (9.071 ppm) was found in one egg of litle tern collected in 1973, and the lowest levels were found in Podiceps eggs, with a range of 0.133-0.138 ppm. From the comparison of the ppm ranges is noteworthy in that the residue levels appear superimposable from phitophagous to predatory species.

Since most eggs were collected in the Biological Reserve of Doñana, which provides a halting place and winter habitat for migratory birds, and since there are no pesticides

TABLE III

Mean levels and ranges (ppm, wet weight) of organochlorine residues in bird eggs collected in the Biological Reserve of Doñana

Date Species No. of eggs		α-HCH	γ-HCH	Heptachl. epoxide	Dieldrin	pp'-DDT	pp'-TDE	pp'-DDE	PCB
1972									
Pochard	3	0.008 (0.002-0.015)	0.023 (0.006-0.039)	0.001	0.001	0.137 (0.057-0.270)	0.005	0.298 (0.100-0.423)	0.655 (0.537-0.787)
Coot	1	0.034	0.014	0.001	0.070	0.060	0.001	0.371	0.056
Purple heron	1	0.018	0.310	0.001	0.012	0.018	0.086	2.007	1.071
1973									
Pochard	4	0.048 (0.034-0.064)	0.097 (0.075-0.134)	0.001	0.001	0.054 (0.034-0.070)	0.040 (0.032-0.050)	0.346 (0.202-0.505)	0.889 (0.854-0.953)
Imperial eagle	5	0.040 (0.020-0.060)	0.233 (0.041-0.546)	0.001	0.066 (0.033-0.132)	0.004	0.546 (0.115-1.102)	1.453 (0.537-3.965)	2.782 (0.599-4.225)

TABLE III (continued)

		α-HCH	γ-HCH	Heptachl. epoxide	Dieldrin	pp'-DDT	pp'-TDE	pp'-DDE	PCB
Spoon duck	3	0.004 (0.003-0.005)	0.009 (0.008-0.010)	0.001	0.005 (0.001-0.009)	0.010 (0.003-0.018)	0.010 (0.005-0.015)	0.702 (0.687-0.714)	0.779 (0.742-0.809)
Avocet	1	0.012	0.030	0.006	0.003	0.034	0.038	0.337	0.133
Podiceps sp.	2	0.037 (0.034-0.040)	0.161 (0.158-0.163)	0.019 (0.019-0.019)	0.001	0.071 (0.058-0.085)	0.034 (0.030-0.038)	1.200 (1.175-1.224)	0.321 (0.318-0.323)
Commun tern	7	0.020 (0.005-0.037)	0.055 (0.009-0.092)	0.013 (0.010-0.019)	0.003 (0.001-0.009)	0.125 (0.039-0.308)	0.016 (0.008-0.027)	0.417 (0.222-0.696)	0.410 (0.163-0.629)
Pratincole	5	0.035 (0.018-0.049)	0.068 (0.054-0.090)	0.009 (0.007-0.014)	0.001	0.112 (0.047-0.188)	0.036 (0.024-0.070)	1.362 (0.773-2.587)	0.603 (0.412-1.070)
Litle tern	8	0.085 (0.040-0.229)	0.148 (0.085-0.299)	0.020 (0.005-0.047)	0.001	0.217 (0.087-0.712)	0.036 (0.017-0.102)	1.347 (0.569-3.285)	3.482 (1.183-9.071)

TABLE III (continued)

		∝-HCH	ϒ-HCH	Heptachl. epoxide	Dieldrin	pp'-DDT	pp'-TDE	pp'-DDE	PCB
1974									
Imperial eagle	1	0.021	0.186	0.001	0.001	0.027	0.402	5.897	1.621
1975									
Lanner	1	0.008	0.029	0.001	0.114	0.214	0.391	2.525	2.637
1976									
Imperial eagle	2	0.005 (0.002-0.007)	0.091 (0.084-0.099)	0.295 (0.265-0.323)	0.294 (0.276-0.314)	0.103 (0.037-0.168)	0.162 (0.054-0.271)	3.192 (2.767-3.617)	5.857 (5.658-6.056)
Black kite	4	0.053 (0.009-0.114)	0.132 (0.044-0.227)	0.001	0.166 (0.093-0.327)	0.344 (0.104-0.623)	1.000 (0.143-1.625)	4.561 (2.435-7.699)	1.520 (0.987-2.001)

TABLE IV

Mean levels and ranges (ppm, wet weight) of organochlorine residues in bird eggs collected in the Provinces of Salamanca (booted eagle) and Cáceres (bustard and imperial eagle)

Date Species No. of eggs		α-HCH	γ-HCH	Heptachl. epoxide	Dieldrin	pp'-DDT	pp'-TDE	pp'-DDE	PCB
1975									
Booted eagle	1	0.015	0.077	0.329	0.247	0.200	0.396	4.321	3.722
Bustard	1	0.017	0.041	0.001	0.039	0.194	0.345	0.697	0.527
1976									
Imperial eagle	2	0.099 (0.016-0.182)	0.524 (0.259-0.790)	0.275 (0.146-0.404)	0.376 (0.325-0.426)	0.173 (0.170-0.177)	0.241 (0.153-0.328)	6.156 (3.111-9.202)	6.609 (5.476-7.742)

for pest control in the Reserve area the pollutants appear to be all imported through water and/or airborne and through migration processes. Pesticides and other pollutants could enter the Reserve either by aerial transport or drainage water since the water systhem of the area forms a more or less closed circuit with the Guadalquivir river. This river is also polluted by low levels of similar residues found in the eggs (HERNANDEZ, GONZALEZ, and BALUJA, 1976). Pesticides are also applied by aerial spraying on rice and olive-planting areas not too far from the Reserve.

According to data summarized in Tables 3 and 4 it appears that residue concentrations decrease in the order PCB > DDT (total) > hexachlorocyclohexanes > cyclodienes. The mean levels of each of the residues found are consistent with the trophic position of the avian species from which eggs were sampled. Accordingly the eggs of raptorial species show the highest residue levels (Fig. 1) followed by other medium predators localized in the middle of the food chain. The phitophagous species show the lowest residue levels as it corresponds to the lower links of the chain.

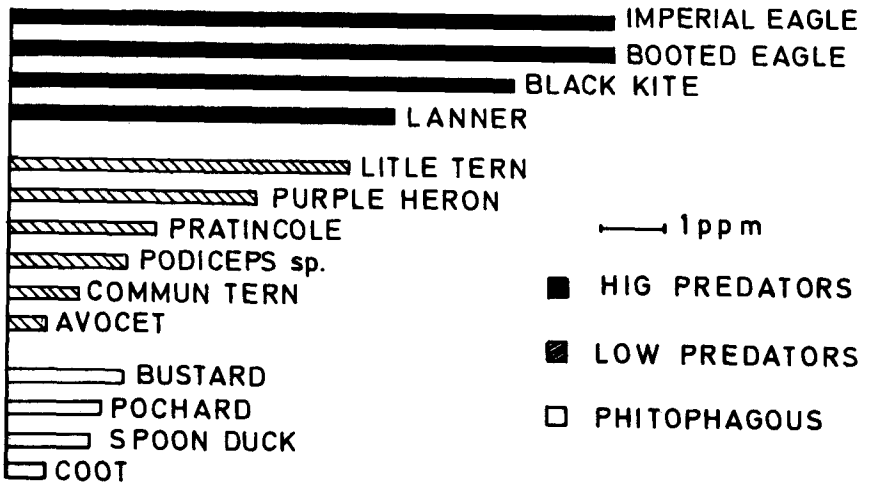

Figure 1. Distribution of mean levels of total organochlorine residues detected in the eggs analyzed.

That the bird population in the area is showing symptoms of decline is presumable because the pollutants found are toxic to the embryo or hatched young, but their

effects on toxicity may not be strictly additive with regard to the quantitative effect induced by a given unit of a chemical. According to FABER and HICKEY (1973), DDE, dieldrin and PCB's are greatly related to eggshell thinning in many species but DDT, TDE, and HCH are not significant factors. However BLUS et al. (1972, 1974) consider that the experimental evidence regarding the ability of PCB's to thin eggshells is conflicting in wild birds although they may be involved in the lowered reproduction success. Nevertheless it is noteworthy that HOORN et al (1973) has measured the eggshell index of eggs collected in Doñana in the spring of 1972 and on comparing with spanish eggs available from Dutch collections they suggest that thinning of the eggshell may have occurred in most species, and since a decline in thickness has been found to coincide with a drop in reproductive success in some of the species studied (duck, peregrine falcon) the same may be true for other species living in the area of the Reserve.

In a previous study (BALUJA and HERNANDEZ, in press) was found that bioconcentration of organochlorine residues in tissues of purple heron living in the Doñana Reserve have increased 20-fold during the course of the 27 months elapsed between the first and the latest collection carried out in 1974. In the present study there was also found to be a general increase in the total amounts of organochlorine residues in eggs during the period 1972-1976. Thus for a typical phitophagous bird like pochard the eggs showed an annual increase of 1.30 but the eggs of a predator like the imperial eagle have an increase of 1.59 for the period 1973-1974 and 1.22 beween 1974 and 1976; this decrease is attributed to pesticide residues because PCB levels had increased during this period. It is also noteworthy that the eggs of the imperial eagle from the Reserve of Doñana contain lower concentrations of residues than those of the same species collected in the Province of Cáceres which appears attributable to pestide application in this area.

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REFERENCES

BALUJA, G., and L.M. HERNANDEZ: Bull. Environ. Contam. Toxicol. (in press).

BALUJA, G., J.M. FRANCO: in Fate of Pesticides in Environment, vol. 6, Ed. A.S. TAHORI, Gordon & Breach Sc. Publ., London 1972, pp 263-272.

BALUJA, G., J.M. FRANCO, M.A. MURADO, and Ma. E. PEREIRO: An. Quím. 66, 157-166 (1970).

BLUS, L.J., A.A. BELISLE, and R.M. PROUTY: Nature, 235, 376-377 (1972).

BLUS, L.J., A.A. BELISLE, and R.R. PROUTY: Pest. Monitoring J., 7, 181-194 (1974).

FABER, R.A., and J.J. HICKEY: Pest. Monitoring J., 7, 27-36 (1973).

HERNANDEZ, L.M., Ma. J. GONZALEZ, and G. BALUJA: Agroquim. Tecnol. Aliment., 16, 279-292 (1976).

HOORN. A.J.W., D.J. BOERWINKEL, and J.H. KOEMAN: in A study on the prossible side-effects of pesticide on the Fauna of the Coto-Doñana in South-West Spain. Communication to the Coto-Doñana Authority, Wageningen 1973.

ONLEY, J.M. and P.A. MILLS: J. Ass. Offic. Agr. Chemists, 45, 983-987 (1962).

REYNOLDS, L.M.: Bull. Environ. Contam. Toxicol., 4, 128-143 (1969).