Organchlorine Pesticides and PCBs Distribution in Tissues of Purple Heron and Spoon Duck from the Biological Reserve of Doñana (Spain)

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In earlier papers (BALUJA et al., 1973, 1974) results were reported from an extensive study on the pollution of abiotic substrata and fauna by persistent organochlorine pesticides and PCBs in some continental and littoral national areas. The current study reports the results obtained from species of Purple Heron (Ardea purpurea) and Spoon Duck (Anas clypeata) collected in the Biological Reserve of Coto Doñana during the period 1972-1974. The first species is sedentary in the Reserve and the second is either partialy migratory or very mobile due to its search for food as a result of weather changes. This Biological Reserve is situated near the mouth of the Guadalquivir river on the right bank, in the South-West of Spain, as it shown in the adjoining map.

Two main considerations were taken into account in selecting the Reserve as a substrate for studying: firstly its ecological significance as one of the most important ornithological reserves of Europe, which must be kept away from organochlorine pollutants which, as it is well known, may affect avian population by overlaping and deleterious influences. The second point is that the Reserve is an area where there is no direct incidence of organochlorine pollution because no chemicals are used in pest control activities. Therefore, it is considered an uncontaminated area. Any occurrence of organochlorine residues can only have been imported through mechanisms of transport related to climatology, geographic factors as well as biotic fluxes.

MATERIALS AND METHODS

Characteristics of samples, preanalytical treatment and residue anlysis. - The purple heron feeds mainly on fish but also on amphibian species and small mammals of the marsh, and occupies one of the higher links in the trophic chain of the Reserve. The spoon duck belongs to a lower trophic level of the same community owing to its herbivorous diet based on seeds, leaves and buds of aquatic plants. The herons were

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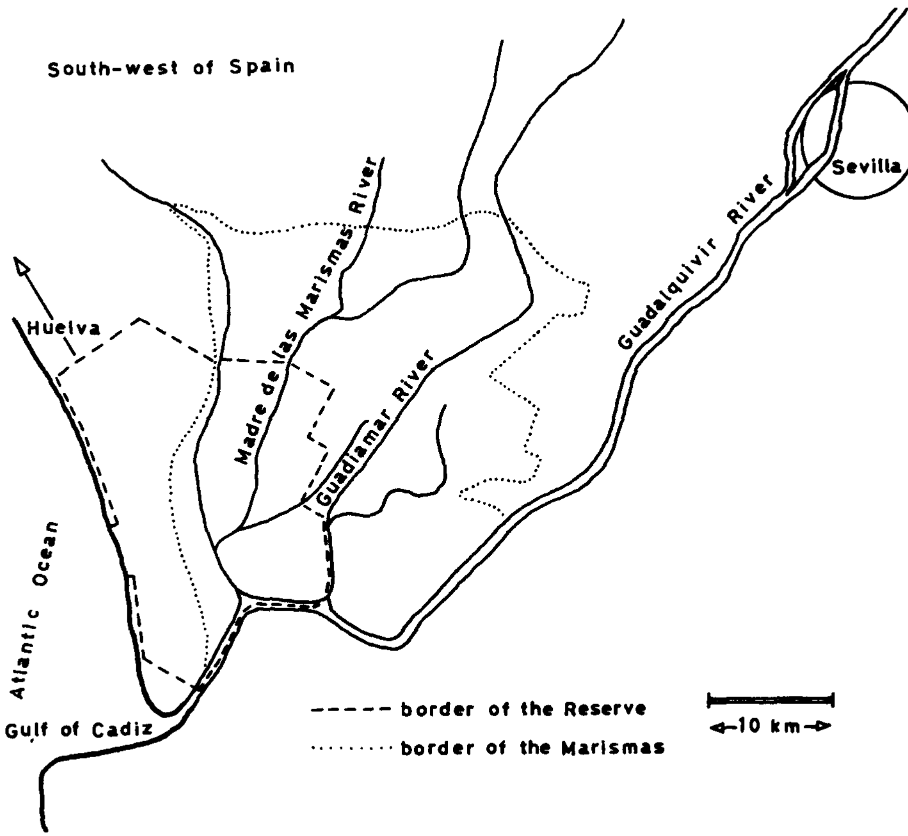
collected in May 1972, September 1973 and July 1974, and the ducks in March and September 1973. Eggs of both species were also collected in 1972 (heron) and 1973 (duck) during the breeding period.



From each specimen samples of muscle, liver, kidney, brain, and gonad were obtained for individual analysis. Collected birds and tissue samples were kept frozen until the pre-analytical treatment which was carried out according to the following steps: homogenization, extraction, partitioning and adsorption chromatography already described in earlier papers (BALUJA et al., 1969 a, b, c, 1970). Identification of organochlorine residues was made by conventional methods of EC-GLC and chemical derivatization also described in the references mentioned above. Parameters for quantitation were as follows: column packing, mixture of 5% DC-200 and 7.5% QF-1 on Chromosorb WHP 80-100 mesh; temperatures, column 200º C, detector 210º C, injector 215º C; nitrogen flow rate 67 ml/min.

RESULTS AND DISCUSSION

Data on quantitative analysis are summarized in Tables I, II, and III. From summarized data two suggestions appear to be obvious: first, if residue levels occur in tissues coming from two species relatively separate in the trophic chain of the Reserve, it is not illogical to suppose that other levels of organochlorine pesticides and PCB residues must not only be present in every component of the biological community established there, but in the abiotic system as well. Second, since there is no chemical industry and/or pesticides for pest control in the Reserve, the pollution appears to be all imported at a regional level. Some probable contributions could be attributed, for example, to water-borne chemicals and migrations. However, it does not appear that migrations may represent an important contribution to the levels of residues found in species of such little mobility as the purple heron, when much lower levels occur in the much more mobile spoon duck, following its natural diet.

None of the individual organochlorine pollutants detected, however, reach accumulations sufficient to cause any rapid decrease in bird populations, as it has already been reported by HOORN et al. (1973). But according to ODUM (1972) the simple occurrence of chronic levels of xenobiotic compounds may be a source of pressure on the energetic flux of the community. It appears, however, that either because of the regularity of the residues' appearance or the accumulation they reach in the tissues, the concentration of pollutants increase in this order: cyclodienes $<$ hexachlorocyclohexanes $<$ DDT group $<$ PCBs. The entrance of cyclodiene pesticide residues in the biological community results to be the lowest and irregular but the hexachlorocyclohexanes are systematicaly found in all sub-samples and, as they are less persistent, it suggests a continuous process of entrance analogous, at least, to the level of its disappearance.

The accumulation of DDT is higher than the other pesticide residues found, the DDE fraction being the major contributing factor to the level of contamination of this group of pollutants, mainly in the purple heron ultimately sampled. However the DDT found is much lower than the level range that STICKEL et al. (1969) associated with the mortality of birds, but DDE accumulation is particularly high in gonads and even in eggs, and in the case of heron eggs, is four times higher than the 0.5 ppm threshold limit, at which level the first symptoms of disfunctions in the process of egg-shell formation arise and the consequent depression of bird fertility (BLUS et al., 1972).

TABLE I.

Mean levels and ranges (ppm wet weight) of organochlorine pesticides and PCBs detected in sub-samples of purple heron

COMPOUNDS	LIVER	MUSCLE	KIDNEY	BRAIN	GONAD
(Sampling date May 1972, 5 specimens, mean weight 476 g)					
α-HCH	0.006 (0.001-0.018)	0.016 (0.003-0.056)	0.043 (0.014-0.072)	0.031 (0.020-0.047)	0.106 (0.091-0.127)
γ-HCH	0.016 (0.002-0.044)	0.026 (0.003-0.066)	0.044 (0.013-0.079)	0.044 (0.029-0.059)	0.106 (0.085-0.129)
Heptachlor	0.006 (0.001-0.022)	0.006 (0.002-0.016)	0.018 (0.009-0.026)	0.013 (0.009-0.015)	ND
Dieldrin	ND	0.006 (0.002-0.030)	ND	ND	ND
p,p´-DDE	0.167 (0.095-0.324)	0.243 (0.126-0.585)	0.227 (0.181-0.304)	0.189 (0.099-0.249)	0.283 (0.214-0.391)
p,p´-TDE	0.022 (0.005-0.058)	0.029 (0.013-0.086)	0.038 (0.021-0.067)	0.024 (0.015-0.041)	0.019 (0.013-0.040)
p,p´-DDT	0.036 (0.011-0.058)	0.059 (0.016-0.138)	0.066 (0.042-0.091)	0.035 (0.023-0.049)	0.090 (0.072-0.100)
PCBs	0.327 (0.104-0.721)	0.558 (0.210-2.132)	0.376 (0.214-0.512)	0.247 (0.202-0.346)	0.593 (0.327-0.691)
(Sampling date September 1973, 1 specimen, weight 335 g)					
α-HCH	0.035	0.265	0.005	0.037	0.095
γ-HCH	0.177	0.461	0.040	0.096	0.226

Table I. (continued)

COMPOUNDS	LIVER	MUSCLE	KIDNEY	BRAIN	GONAD
p,p´-DDE	1.318	2.103	0.596	0.218	0.891
p,p´-TDE					0.543
p,p´-DDT	0.325	0.504	0.130	0.092	2.364
PCBs	2.287	3.249	1.489	1.235	18.765
(Sampling date July 1974, 2 specimens, mean weight 487 g)					
α -HCH	0.011 (0.010-0.013)	0.020 (0.012-0.028)	0.014 (0.012-0.016)		0.055 (0.033-0.077)
γ -HCH	0.079 (0.067-0.091)	0.053 (0.033-0.073)	0.060 (0.040-0.081)		0.205 (0.128-0.281)
Heptac. epox.	0.031 (0.022-0.039)	0.007 (0.007-0.008)	0.017 (0.015-0.019)		ND
Dieldrin	ND	ND	ND		0.134 (0.001-0.267)
p,p´-DDE	20.982 (9.491-32.473)	3.809 (3.543-4.076)	9.866 (5.254-14.479)		24.358 (17.986-30.731)
p,p´-TDE	0.281 (0.108-0.455)	0.060 (0.051-0.068)	0.173 (0.136-0.209)		1.884 (0.827-2.942)
p,p´-DDT	0.364 (0.261-0.559)	0.307 (0.138-0.354)	0.134 (0.130-0.138)		2.372 (1.636-3.108)
PCBs	7.453 (1.052-13.854)	2.085 (0.674-3.496)	2.833 (0.791-4.875)		11.592 (6.047-17.138)

TABLE II.

Mean levels and ranges (ppm wet weight) of organochlorine pesticides and PCBs detected in sub-samples of spoon duck.

COMPOUNDS	LIVER	MUSCLE	KIDNEY	BRAIN	GONAD
(Sampling date march 1973, 8 specimens, mean weight 580 g)					
α-HCH	0.022 (0.005-0.036)	0.022 (0.013-0.048)	0.083 (0.065-0.102)	0.026 (0.007-0.045)	1.878 (0.147-3.609)
γ-HCH	0.065 (0.013-0.122)	0.056 (0.032-0.112)	0.257 (0.214-0.301)	0.070 (0.050-0.090)	2.525 (1.414-3.490)
Dieldrin	0.003 (0.002-0.020)	0.006 (0.003-0.021)	ND	ND	ND
p,p´-DDE	0.252 (0.070-0.494)	0.292 (0.090-0.483)	0.357 (0.146-0.568)	0.079 (0.063-0.094)	0.810 (0.804-0.816)
p,p´-TDE	0.061 (0.008-0.215)	0.076 (0.008-0.190)	0.087 (0.031-0.143)	0.010 (0.006-0.015)	0.575 (0.143-1.014)
p,p´-DDT	0.126 (0.004-0.674)	0.058 (0.021-0.103)	0.097 (0.042-0.153)	0.073 (0.026-0.119)	6.911 (0.534-13.288)
PCBs	0.830 (0.198-1.558)	0.929 (0.307-1.700)	0.923 (0.721-1.125)	0.487 (0.346-0.629)	9.351 (2.931-15.772)

Table II. (continued)

COMPOUNDS	LIVER	MUSCLE	KIDNEY	BRAIN	GONAD
(Sampling date September 1973, 3 specimens, mean weight 406 g)					
α -HCH	0.033 (0.013-0.057)	0.018 (0.016-0.023)	0.009 (0.007-0.012)	0.051 (0.041-0.061)	
γ -HCH	0.045 (0.019-0.080)	0.029 (0.023-0.032)	0.018 (0.014-0.021)	0.073 (0.067-0.079)	
Heptac. epox.	0.035 (0.043-0.135)	ND	ND	ND	
Dieldrin	0.059 (0.015-0.089)	0.012 (0.013-0.023)	0.018 (0.013-0.029)	ND	
p,p´-DDE	0.150 (0.065-0.231)	0.154 (0.095-0.204)	0.090 (0.070-0.114)	0.089 (0.080-0.096)	
p,p´-TDE	0.024 (0.008-0.036)	0.008 (0.004-0.012)	0.006 (0.004-0.007)	ND	
p,p´-DDT	0.106 (0.067-0.132)	0.027 (0.016-0.042)	0.028 (0.021-0.044)	0.045 (0.036-0.051)	
PCBs	1.087 (0.590-1.458)	0.576 (0.451-0.787)	0.856 (0.714-0.929)	1.811 (1.724-1.921)	

Heptac. epox. = Heptachlor epoxide; ND = none detected

TABLE III.

Mean levels and ranges (ppm wet weight) of organochlorine pesticides and PCBs detected in eggs of purple heron (2 specimens) and spoon duck (3 specimens)

COMPOUNDS	Purple heron (May 1972)	Spoon duck (May 1973)
α -HCH	0.018 (0.015-0.021)	0.004 (0.003-0.005)
γ -HCH	0.310 (0.290-0.330)	0.010 (0.009-0.010)
Dieldrin	0.012 (0.009-0.015)	0.005 (0.001-0.009)
p,p´-DDE	2.077 (2.040-2.114)	0.702 (0.687-0.714)
p,p´-TDE	0.086 (0.084-0.088)	0.010 (0.005-0.015)
p,p´-DDT	0.018 (0.012-0.024)	0.010 (0.003-0.018)
PCBs	1.071 (1.003-1.139)	0.779 (0.742-0.809)

Regarding PCBs it is evident that they constitute the main source of pollution of all organochlorine residues found (Tables I to III). This fact has been broadly reported in the literature on wildlife contamination. Various authors (VOS & KOEMAN, 1970, DAHLGREN et al., 1972) have found a positive correlation between death and PCB levels in the brains of birds when residue ratios are in the range of 200-400 ppm. This correlation is less strict when other tissues are considered even though some relationship may exist as in the case of mortalities observed in bird populations having lower accumulations (HOLDGATE, 1971). However, it seems that PCB effects are analogous to those produced by DDE on the reproductive mechanisms, because even though they are not inhibitors of carbonic anhydrase they can however stimulate the production of liver hydroxilases to reduce the levels of circulating estrogens (RISEBROUGH et al., 1968).

It seems obvious then to consider that the success of bird reproduction may depend, in one way on the total quantity of DDE and PCBs present, and also of dieldrin, in spite of its individual low level, but as PEAKALL showed (1967) it plays an important role in the estrogen balance. From the observation of the distribution of all organochlorine pollutants in the tissues studied, it can be seen that residues are mainly accumulated in gonads and at a lower rate in the brain, though the unexpectedly high values in liver may suggest some recent mobilization of fat. Assuming that the correlations between poisoning and organochlorines residue levels in tissues are mainly based on the accumulation rate in the brain, it should be possible to assume that any irreversible deterioration of a bird population through an overlapping depression of its fertility is not necessarily accompanied by mass mortalities of individual adults.

The increases of total residues are very significant in the purple heron from the first to the third period of collecting (Table I) but the increase is much smaller in the case of ducks (Table II). This fact may be due, at least in part, to the shorter interval between the two collectings of ducks, undertaken during the period of the lowest increase in the heron, but perhaps even more so by the position of ducks in the food chain of the marsh of the Reserve. On the other hand, the residue build-up in heron species reaches a 20-fold increase during the course of the 27 months between the first and third collections. This bioconcentration factor appears unexpectedly high and suggests the need for a more extended study as evidently the growing state of pollution will affect the biological balance of the Reserve.

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