### ORGANOCHLORINE EXPOSURE IN PEREGRINE FALCON {Falco peregrinus) EGGS AND ITS AVIAN PREY {Columba livia).

#### L. R. Bordajandi, R. Merino, and B. Jimenez

Dept. of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, CSIC Juan de la Cierva 3. 28006 Madrid. Spain

#### Introduction

In the last five decades many wildlife populations all over the world have experienced severe declines. Many of these declines sometimes have not been satisfactorily explained by natural biological events. It is well known that some chemicals, in particular organochlorines, have the ability to interfere with the development of the reproductive, endocrine, immune and nervous systems of embryos. It has been reported in many studies the decline of bird populations due to the increase in the use of chemical pesticides, which they bioaccumulate from the preys they feed'. For example, the declining reproductive success of peregrine falcons (Falco peregrinus) breeding in the Arctic in the early 1970s has been attributed to organochlorine contamination, particularly DDE<sup>2</sup> and, in other studies, it has been reported to be caused primarily by urban and agricultural insect control measures<sup>3,4</sup>. This could be the case of peregrine falcons in Spain. Peregrine falcon populations in Central Spain declined dramatically during the last ten years. Fernandez et al.<sup>5</sup> reported the presence of considerable amounts of organochlorine residues (PCBs and DDTs) in the area where the peregrine falcon population is being studied. Of particular concern is the fact that DDT levels found in the area studied were consistently higher than its metabolite DDE, indicating a recent use ofthis organochlorine insecticide in the area. The present study provides preliminary data from a more extended research project focused on the study of the implications of organochlorine residues in the decline observed in peregrine falcon populations in the Center of Spain. The current status of contaminant residues in peregrine falcon eggs and their avian prey species, feral pigeons (Columba livia), in Central Spain and its significance for the recovery of the raptor population is examined.

#### Materials and Methods

#### Studv area and sampling.

The study area is located in the province of Madrid (Spain) and correspond to the Madrid Southeast Regional Park, which was declared a protected zone by the Madrid Regional Government in 1994. It is important to note that this area traditionally has received a high impact from urban, industrial and agricultural activities.

Unhatched eggs of peregrine falcon (*Falco peregrinus*) were obtained from all the nest controlled in the study area during the breeding season of 2000. Eggs were transported to the laboratory and frozen at -80 °C until analysis. Prey species of the peregrine falcon are mainly feral pigeons (Columba livia), which represents about the 80% of the diet. A minimum number of 6 pigeons were collected in two different zones of the study area, and two pools per zone were prepared, corresponding to liver tissue and fat tissue. Fat and liver-pooled samples were kept frozen at -80°C until analysis.

ORGANOHALOGEN COMPOUM)S Vol. 52 (2001) 139

#### Extraction and Clean-up

The extraction of PCBs and DDTs involves a solid phase matrix dispersion (SPMD) procedure. Approximately 3g of freeze-dried egg or lg of fresh tissue in the case of liver and fat were used for analysis. All samples were ground in a mortar with anhydrous sodium sulphate and were extracted with a mixture acetone: hexane (1:1, v/v). Further clean up and lipid removal was achieved by using acid and basic modified silica gel multilayer columns<sup>6</sup>. The lipid content was determined gravimetrically.

Final fractionation among the studied compounds and other possible interferences was achieved by using Supelclean<sup>™</sup> Supelco ENVI<sup>™</sup>-Carb tubes as described elsewhere<sup>7</sup>. Three fractions were eluted. The first fraction contained the bulk of PCBs and DDTs. The second and third fraction contained non-*ortho* substituted PCBs and PCDD/Fs, respectively. The results of the analysis of the first fraction eluted are presented in this paper.

Identification and Ouantification.

Analyses were performed using a Hewlett Packard 6890 equipped with a  $^{63}$ Ni  $\mu$ -electron capture detector. A DB-5 fused silica capillary column (60m  $x$  250 $\mu$ m and 0.25 $\mu$ m film thickness) was used. The carrier gas was Nitrogen at a head pressure of 192.2 Kpa. Detector and injector temperatures were 300°C and 270°C respectively. The following over temperature program was used: initial temperature 80°C held for 2 min., 80 to 185°C at 30°C/min., 185 to 230°C at 1.5°C/min., and 230 to 270°C at 5°C/min. The final temperature was held for 25 min. TCN and PCB # 209 were used as internal standards. The following organochlorines were analyzed in peregrine falcon eggs and pigeons: DDT, TDE, DDE; and PCB congeners with Ballschmiter-Zell (BZ) numbers: 28, 52, 95, 101, 123, 149, 118, 114, 153, 132, 105, 13:?, 183, 167, 156, 157, 180, 170, 189 and 194.

#### Results and Discussion

All results are reported on a wet weight basis (ww). Total PCB levels in eggs ranged from 429 to 3335 ng/g (ppb). PCB concentrations in egg samples were higher than those found in pigeon tissues. In the case ofthe preys studied clear differences regarding total levels were found between fat and liver. In liver, PCB levels ranged from 22 to 53 ng/g while in fat tissue levels ranged from 120 to 232 ng/g. This fact could be explained considering that organochlorine are highly lipophilic, so the highest levels should be expected in fat tissue.

Accumulation patterns were also different when comparing falcons and preys. In egg samples PCB nos. 180, 153 and 138 accounted for the highest percentage of the total PCB content (75 %), while the rest of PCBs were found in a very low percentage. This was alsc' found is eggs from white stork (Ciconia ciconia) and black kite (Milvus migrans) studied in the South of Spain<sup>8</sup>. Concerning accumulation pattems in preys, the most abundant PCBs observed in eggs were also found in pigeon tissues, but the ratios of lower chlorinated PCB congeners (tri- to penta-) to total PCBs were larger than in the raptors, as shown in Figure 1. This indicates that the composition of PCB congeners would reflect the differences of feeding habits and xenobiotic metabolizing systems among both species studied as reported by Hoshi et al<sup>9</sup>.

In all samples analyzed DDT and its two main metabolites, DDE and TDE, were detected. Egg samples presented higher values of these compounds ( $\Sigma$ DDTs ranging from 0.226 and 0.775 µg/g) than preys ( $\Sigma$ DDTs ranging from 0.004 and 0.027  $\mu$ g/g). In the case of eggs, DDE contributed with a 99% to the total DDTs content, while in preys, DDE contributed with a 69%. Comparing DDT levels between liver, fat tissue and eggs, it is significant that in liver samples it represents a 42% of the total DDTs (Fig 2). As liver is the organ where DDT is metabolized, higher

#### ORGANOHALOGEN COMPOUNDS Vol. 52 (2001) 140

concentrations could be found, while in eggs and fat, the main products found are the metabolites, and mainly the most persistent, DDE. The ratio DDE/DDT found indicates that this banned insecticide was not recently used in the studied area.





Some studies on passerines have documented no apparent effects on reproductive success in passerines with OC compounds in the  $\mu$ g/g range. Elliot et al.<sup>10</sup> found no reproductive effects in a population of American robins (*Turdus migratorius*) with eggs contaminated with p, p'-DDE at levels of 80 ug/g. Custer et al.<sup>11</sup> found that the concentration of PCBs of up to 10 ug/g in tree swallow (Tachycineta bicolor) eggs did not seem to affect hatching success. In contrast McCarty and Secord<sup>12</sup> documented reduced nesting quality, a trait correlated with lower reproductive success, in swallows contaminated with PCBs in the  $5-25 \mu g/g$  range. Peregrine falcons have been documented to be very sensitive to the effects of DDE; estimates of the levels at which population may be impacted are of 15-20 ppm for peregrines<sup>13</sup>. Henny et al.<sup>14</sup> reported levels of organochlorine pesticides and PCBs in falcon eggs from Russia during the period 1992-1993 and a high DDE concenfration (27.3 ppm, ww) in the Peregrine Falcon eggs raised concem for the species in European Russia south of the Arctic Circle.



Fig 2. DDTs pattern in eggs and pigeon tissues analyzed.



Concerning DDE and DDT levels, those found in this study were lower than those found for peregrine falcon in Arizona<sup>15</sup> (DDE = 2329 ng/g ww and DDT = 19 ng/g ww) and Sweden<sup>16</sup>  $(\Sigma PCBs = 23-57$  ppm and DDE= 14-22 ppm). 1 ppm DDE is the more conservative level considered sufficient in prey to produce decreased productivity in peregrines<sup>17</sup>. Although a number of organochlorine contaminants were found in eggs and preys in this stucy, concentrations were all below known effect level.

#### Acknowledgements

This study was funded by SEO (Sociedad Española de Ornitología) Birdlife.

#### References

1. Colbom, T. (1995). Environ. Health Perspect. 103, 3.

2. Risebrough, R.W., Springer, A.M., Temple, S.A., White, CM., Albuquerque, J.L.B., Bloom, P.H., Fyfe, R.W., Kirven, M.N., Luscombe, B.A., (1990). Rev. Bras. Biol. 50(3): 563.

3.Cade, T.J., Lincer, J.L., White, CM., Roseneau, D.G., Swartz, L.G. (1971). Science 172: 955. 4.Peakall, D.B. (1974). Science 183: 673.

5. Fernandez, M., Cuesta, S. Jimenez, 0., Garcia, M.A., Hernandez, L.M. Marina, M.L., Gonzalez, M.J. (2000) Chemosphere 4\: 801.

6. Ramos, L., Eljarrat, E., Hemdndez, L.M., Rivera, J and Gonzalez, M.J. (1999) Chemosphere 38: 2577.

7. Molina, L., Cabes, M., Diaz-Ferrero, J., Coll, M., Marti, R., Broi:o-Puig, F., Cornelias, L., Rodriguez-Larena, M.C. (2000) Chemosphere 40: 921.

8. Jimenez, B., G6mara, B., Baos, R., Hiraldo, P., Eljarrat, E., Rivera., J., Gonzalez, M.J. (2000) Organohalogen compounds 46:542.

9. Hoshi, H., Minamoto, N., iwata, H., Shiraki, K., Tatsukawa, R., Tanabe, S., Fujita, S., Hirai, K. and Kinjo, T. (1998) Chemosphere 36: 3211.

10. Elliot, J.E., Martin, P.A., Arnold, T.W., Sinclair, P.H. (1994). Arch. Environ. Contam. Toxicol. 26,435.

11. Custer, CM., Custer, T.W., Allen, P.D., Stromborg, K.L., Melacom, M.J. (1998). Environ. Toxicol. Chem. 17, 1786.

12. McCarty, J.P., Secord, A.L. (1999). The Auk 116, 55.

13. Fyfe, R.W., Risebrough, R.W. Monk, J.G., Jarman, W.M., Anderson, D.W., Kiff, L.F., Lincer, J.L., Nisbet, I.C.T., Walker, W., Walton, B.J. (1988). In : Cade, T.J., Enderson, J.H., Thelander, C.G., White, CM. (eds) Peregrine falcon populations. Their management and recovery. The Peregrine Fund Inc., Boise, ID.

14. Henny, C.J., Galushin, V.M., Dudin, P.I., Khrustov, a.V., Mischenko, A.L., Moseikin, V.N., Sarychev, V.S., Turchin, V.G. (1998). J. of Raptor Research 32(2): 143.

15. Ellis, D.H., DeWeese, L.R., Grubb, T.G., Kiff, L.F., Smith, D.G., Jarman, W.M., Peakall, D.B. (1989) Bull. Environ. Contam. Toxicol 42: 57.

16. Lindberg, P., Odsjb, T. and Reutergardh, L. (1985) Arch. Environ. Contam. Toxicol. 14: 203.

17. Banasch, U., Goosein, J.P., Riez, A.E., Casler, C, Barradas, R.S.. (1992). Canadian Field-Naturalist. 106(4): 493.

#### ORGANOHALOGEN COMPOUNDS Vol. 52 (2001) 142