CURRENT CONCENTRATIONS OF ORGANOCHLORINE COMPOUNDS (PCDDs, PCDFs, PCBs AND DDTs) IN PEREGRINE FALCONS AND THEIR AVIAN PREY. A CASE STUDY IN CENTRAL SPAIN

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Introduction

Adverse effects of organochlorine compounds such as Polychlorinated Biphenyls (PCBs), Polychlorinated Dibenzo-p-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and organochlorine insecticides in wildlife had been widely documented in the literature in the past decades[1,2]. In particular these effects had been documented for some particularly sensitive and emblematic species such as the peregrine falcon[3]. During the last years a decline has been detected in peregrine falcon (*Falco peregrinus*) populations from Central Spain[4]. It is important to note that this area traditionally has received a high impact from urban, industrial and agricultural activities. Fernández et al.[5] reported the presence of considerable amounts of organochlorine residues (PCBs and DDTs) in the area.

It has been reported in many studies that the decline of bird populations is due to the increase in the use of chemical pesticides, which they bioaccumulate from the preys they feed[1]. That is the reason to study these contaminants in falcon preys, particularly in pigeons, because they represent about the 80 % of the total diet of these raptors.

The current status of contaminant residues in peregrine falcon eggs and their main avian prey species, feral pigeons (*Columba livia*), in the Regional Park of Southeastern Madrid (RPSM) and its significance for the recovery of the peregrine falcon population is examined and compared to a control area.

Materials and Methods

Study area

The study area is located in the province of Madrid (Spain) and corresponds to the Regional Park of Southeastern Madrid (RPSM), which was declared a protected zone by the Madrid Regional Government in 1994. The control area with a presumably lower pollution impact was selected in the province of Guadalajara located eastern of Madrid.

Samples

During the breeding season of 2000 and 2001 eight unhatched eggs of peregrine falcon (*Falco peregrinus*) were obtained from 25 nest controlled for the present study, including both the presumably polluted area which includes the RPSM and the control area.

Unhatched eggs were transported to the laboratory and stored at –80 ºC until analysis.

Approximately 3 grams of lyophilised eggs were used for analysis. Prey species of the peregrine falcon, feral pigeons (*Columba livia*), were collected from different sites in the RPSM, liver was taken and frozen at –80 ºC. About 3 grams of fresh liver were taken for residue analysis.

Analytical determination

The extraction of PCDD/Fs, PCBs and DDTs involved a Solid Phase Matrix Dispersion (SPMD) procedure. Fractionation among the analytes of interest and other possible interferences was achieved using Supelclean™ Supelco ENVI™-Carb tubes as described elsewhere[6]. Three fractions were eluted: the first fraction contained the bulk of PCBs and DDTs; the second and third fractions contained non-*ortho* substituted PCBs and PCDD/Fs, respectively.

Resolution and quantification of mono-*ortho* PCBs and DDTs was carried out by HRGC-ECD using a Hewlett Packard 6890 GC equipped with a ^{63}Ni µ-electron capture detector. A DB-5 fused silica capillary column (60 m x 250 µm and 0.25 µm film thickness) was used. The carrier gas was nitrogen at a head pressure of 192.2 Kpa. Detector and injector temperatures were 300 ºC and 270 ºC, respectively. Resolution and quantification of PCDDs, PCDFs and non-*ortho* PCBs were performed by HRGC-HRMS by using a VG AutoSpec Ultima (VG Analytical, Manchester, UK) coupled to a Fisons Series 8000 (8060) Gas Chromatograph. A minimum resolution of 10,000 was used when operating with the HRMS instrument. A fused silica capillary DB-5 column (60 m, 0.25 mm id., 0.25 mm film thickness, J&W Scientific, USA) and a DB-DIOXIN column were used. The carrier gas was helium at a column head pressure of 175 Kpa. Methods blanks were routinely analysed, and low contributions were detected.

Results and discussion

PCDDs, PCDFs, PCBs and organochlorine pesticides levels in eggs of peregrine falcon

Almost in all the eggs analysed, all the seventeen 2,3,7,8-substituted PCDDs and PCDFs were found. Total PCDD/Fs levels ranged between 6.67 and 8.32 pg/g on a wet weight basis (WW) in the control area (Guadalajara). The concentration range in the control area is quite similar to that found in the RPSM area where total PCDD/Fs levels ranged from 12.69 to 19.10 pg/g (WW). Regarding the specific 2,3,7,8-substituted congener pattern, it was noticeable that the 2,3,4,7,8-PeCDF was the most abundant congener with percentages ranging from 23 % to a 40 %.

Non-*ortho* PCBs were detected in all the eggs analysed. In the control area total non-*ortho* PCBs levels ranged from 131.68 to 163.10 pg/g (WW), being the most abundant congener PCB #126, followed by PCB #77 and PCB #169. In the RPSM non-ortho PCB levels ranged from 246.50 to 694.18 pg/g (WW), being slightly higher than in the control area.

In the case of *ortho*-PCBs, total levels in the control area ranged between 202.56 and 288.40 ng/g on a wet weight basis (WW) while in the RPSM area total ortho-PCBs ranged from 429.76 to 3335.16 ng/g (WW). In all eggs the most abundant PCBs were #180 and # 153, accounting with an 80% to the total. Concentrations of total PCBs in all the eggs analysed were lower than levels (> 4,000 ng/g) shown to cause reduced hatching, embryo mortality, and deformities in birds[7]. However some of them exhibited concentrations near the threshold value and this should be a cause of concern.

DDT and its main metabolite (DDE) were found in all the eggs analysed. DDT levels were low in both areas studied. In the control area DDT levels ranged from 0.9 to 1.1 ng/g (WW) while in the RPSM, DDT levels ranged between 3.1 to 4.5 ng/g (WW). However the situation was different regarding DDE which levels ranged between 254 and 270.1 ng/g (WW) in the control area. DDE levels were considerably higher in samples from the RPSM ranging from 222.8 ng/g to 1911.9 ng/g (WW). It was observed that some of the eggs from the RPSM exceed the levels associated with reproductive impairement[8]. These results clearly indicate that DDE is still present in the study area at high

concentrations as reported in previous studies conducted in this area[5,9]. This finding suggest a possible risk for the peregrine falcon populations feeding in the studied area taking into account that this species had been shown to be particularly sensitive to DDE effects[3].

2,3,7,8-TCDD equivalents (TEQs) were estimated for PCDD/Fs congeners and dioxin-like PCBs with an assigned TEF value, based on the Bird Toxic Equivalency Factors (TEFs) reported in 1998 by the World Health Organisation[8]. Total TEQs in all eggs analysed ranged between 12.1 and 14.4 pg/g (WW) in the control area, while in the RPSM the range was 20.7 - 53.9 pg/g (WW). In all eggs analysed, the highest contribution to the total TEQs corresponded to non-*ortho* PCBs, with a percentage contribution between a 63 and a 78 % followed by the PCDFs, which ranged between 10 and 22 %.

Total PCDDs, PCDFs, PCBs and organochlorine pesticides in pigeons from the RPSM.

In pigeon's liver, total PCDD/F levels ranged from 5.1 to 11.2 pg/g (WW). This value indicate that PCDDs and PCDFs do not contribute to a high pollution input in pigeons in the study area, even if it had been reported PCDD/Fs pollution in the area[10]. In all the samples studied the most abundant congener was the OCDD accounting with 30 % to the total PCDD/F levels, followed by 1,2,3,4,6,7,8-HpCDD which represented a 12 %. In all cases, the levels of PCDDs were higher than those of PCDFs.

The non-*ortho* PCBs were detected in all pigeon livers. Total non-ortho PCB levels ranged between 22.82 to 92.20 pg/g (WW). The most abundant congener was PCB #77, followed by PCB #126 and PCB #169.

Total *ortho* substituted PCBs concentrations ranged from 0.58 to 53.60 ng/g (WW). Among these, the most abundant PCBs were those presenting a low chlorination degree, such as PCBs #28, #52, #95, #101, #118, #123, #149, accounting to the total PCB levels with up to 62 %. This congener pattern is quite different from those observed in eggs from peregrine falcon where PCBs #153 and #180 exhibited the highest levels.

Total calculated TEQs ranged from 2.54 to 6.22 pg/g (WW). The major contribution to the total TEQs came from non-*ortho* PCBs (range between 42.50 and 76.85 %), followed by PCDFs with a contribution to total TEQs between ranging from 13.3 % to 31.9 %.

DDT levels ranged from 0.01 to 1.6 ng/g (WW) while in the case of DDE this range was between 0.02 and 9.7 ng/g (WW).

Considering data obtained in this study, levels of PCCDs and PCDFs found in eggs from peregrine falcon do not seem of concern. However PCBs and organochlorine pesticides, specially DDE showed levels which could be of risk for this species. All the organochlorine compounds studied in feral pigeons do not showed levels of concern for pigeons. However if we consider that pigeons constitute the 80% of the diet of a peregrine falcons studied and considering the biomagnification phenomena, it could be explained the main route of exposure to these organoclorines in peregrine falcons in the area studied.

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