### PRELIMINARY EVALUATION OF ORGANOCHLORINE CONTAMINANTS (PCDDs, PCDFs, PCBs AND DDTs) IN BIRDS FROM BAJA CALIFORNIA, MEXICO

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#### Introduction

In the last five decades many wildlife populations all over the world have experienced severe declines. 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 by urban and agricultural insect control measures<sup>1-3</sup>. Potentially and estrogenic pesticides that are currently in use on agricultural crops throughout the state of Baja California include atrazine, synthetic piretroids, etc. Additionally, persistent pesticides with known or suspected estrogenic and antiandrogenic activity, such as DDT and its metabolites, were used heavily on vegetable crops in Baja before their use was banned in the 1970/80s<sup>4.5</sup>.

In 2000, we initiated studies of the effects of agricultural activities on birds at Baja California, Mexico. The studies initially considered a broad array of inorganic and organic chemicals that were known or suspected to occur in the area. The current status of contaminant residues in *Passer domesticus* and *Columbina passerina* in South Baja California is examined. Although persistent pesticides have decreased in use since the last 20-30 years because they have been officially prohibited, we suspected they have been illegally used for spraying crop fields at the present. This study presents preliminary information attempting to evaluate the current status of organochlorine contaminants on wildlife species of Baja California Sur.

#### **Materials and Methods**

#### Sampling sites and Bird Survey

The study sites were located primarily in southern Baja California. Effort was made to select sites of each type distributed across all the area. Chametla and Centenario cultivated areas (ca.  $24^{\circ}$  03' N;  $110^{\circ}$  30' O) are located near La Paz town. Tomato, chili, alfalfa, maize and other vegetables are the main crop fields. The Valle de Santo Domingo study area is located almost in the middle portion of the state of Baja California Sur, Mexico ( $24^{\circ}$  50' –  $25^{\circ}$  30' N;  $111^{\circ}$  30' –  $112^{\circ}$  10' O) with a land cultivated area of approximately 34,120 ha. Crop fields include a variety of vegetables (chickpea, maize, kidney bean, chili, and sorghum) and all of them receive high amounts of pesticides.

During June to September 2000 and February to September 2001, we used a net-trapping method to catch birds. Six equal sized mist nets were placed at the edge of crop fields, inside them and near water sources. We selected only Common-ground doves (*Columbina passerina*) and House sparrows (*Passer*)

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*domesticus*) birds to evaluate the levels of pesticides and the potential effects on birds associated to crop fields in Baja California. Both species were common in the study area. Common-ground doves are seed eaters and forages frequently inside crop fields, while House sparrows are omnivorous foraging also through field crops and small ranches inserted inside the cultivated areas. Once the birds were collected, liver and fat content was taken and stored at -35 °C until analysis.

#### Analytical determination

Liver was used for residue analysis. Pooled samples were prepared for each species to be studied, consisting of approximately 25 individuals per species.

Approximately 3 grams of each pooled sample were used for analysis. 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 SupelcleanTM Supelco ENVITM-Carb tubes as described elsewhere<sup>6</sup>. 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 were carried out by HRGC-ECD using a Hewlett Packard 6890 GC equipped with a 63Ni  $\mu$ -electron capture detector. A DB-5 fused silica capillary column (60 m 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. Resolution and quantification of PCDDs, PCDFs and co-planar PCBs were performed by HRGC-HRMS 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. Methods blanks were routinely analyzed, and low contributions were detected. 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.

#### **Results and Discussion**

#### Total PCDDs, PCDFs, PCBs and organochlorine pesticides

Total PCDD/F levels in both species studied in general was low, being the highest levels found in house sparrows (20.76 pg/g on a wet weight basis (WW)) while in the case of common-ground doves total PCCD/F levels were 7.74 pg/g (WW).

Total levels for co-planar PCBs (#77, 126 and 169) found in common-ground doves were of 253.62 pg/g (WW) being PCB #77 the most abundant followed by PCB #126 and PCB #169. In the case of house sparrows, total co-planar PCBs were 58.36 pg/g (WW), being PCB #77 the most abundant followed by PCB #126 and PCB #169 as found in common-ground doves.

Total levels of the remaining PCBs analyzed (# 28, 52, 95, 101, 123, 149, 118, 114, 153, 132, 105, 138, 183, 167, 156, 157, 180, 170, 189 and 194) were 248.64 ng/g (WW) in common-ground doves, while in house sparrows were 45.43 ng/g. PCB pattern found in both species studied is shown in Figure 1. It can be observed that the lower chlorinated PCB congeners (tri- to penta-) contributed the most to total PCBs. This suggest that the composition of PCB congeners would reflect the differences of feeding habits and xenobiotic metabolizing systems among different species, as reported by Hoshi et al<sup>7</sup>. PCB values in this study do not suggest that industrial inputs of PCBs in the study area are important.

DDT and its main metabolite (DDE) were found in both species studied. Levels in common-ground doves were not high (34,04 ng/g for DDE and 1.35 ng/g for DDT). However it was noticeable the case

of house sparrows which exhibited levels of DDT of 0.48 ng/g while DDE levels were 3,668.72 ng/g (WW). This value is near the threshold considered for reproductive impairment in birds<sup>8</sup>.

#### Calculated TEQs for PCDDs and PCDFs and PCBs

2,3,7,8-TCDD equivalents (TEQs) were estimated for PCDD/F 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<sup>9</sup>. Total TEQs (considering PCDDs, PCDFs and PCBs with a known TEF) where higher in common-ground doves than in house sparrows, with a value of 15.11 pg/g (WW) and 5.79 pg/g (WW) respectively. In both species studied it was found that the largest percentage contribution to total toxicity came from coplanar PCBs, with a percentage contribution of 54 % in house sparrows and 88.6 % in common-ground doves. Contribution to total TEQs coming from PCDDs and PCDFs were lower than that of coplanar PCBs. Finally it was observed that mono-ortho PCBs contributed less than 1 % to total TEQs in both species studied.

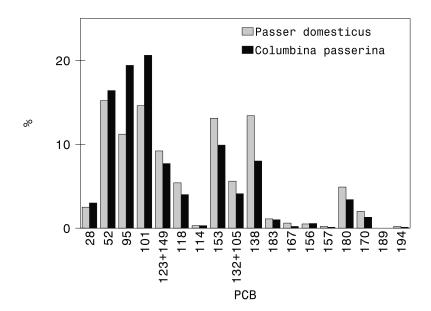


Figure 1. PCB accumulation pattern in house sparrows and common-ground doves.

These preliminary results obtained in birds from Baja California indicate that industrial inputs of PCBs or PCDDs and PCDFs in the study area are not important. However the high levels of DDE found in house sparrows reflect suggests that DDE is still present in the study area at high concentrations. Potential sources of DDE in the study area are probably due to a heavy use of DDT in the past. It is difficult to ascertain the effects of DDE in the populations of the species studied since no previous studies on contaminants and reproduction in birds nesting in the area studied are available. The preliminary results presented here confirm the initial suspect of this study and suggest the importance of further monitoring of organochlorines in Baja California Sur. In addition we would like to note that the species studied demonstrated to be a good bioindicator organism for organochlorine exposure.

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