PCDD/PCDF, PCB AND CHLORINATED PESTICIDES IN EGGS OF WILDLIFE BIRDS OF PREY FROM NORTH RHINE-WESTPHALIA, GERMANY 2000 – 2009

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Introduction

Since birds of prey are on the top of the food-chain, their eggs are an excellent source of material to keep an eye on environmental contaminants. The collection of unbreeded or dead eggs is an easy way to get biotic material from wildlife birds. The contents of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF), polychlorinated biphenyls (PCB) and assorted chlorinated pesticides were analysed in 110 samples of unbreeded or dead eggs of several species of birds of prey from 2000 – 2009. The samples were collected in North Rhine-Westphalia, Germany in rural as well as in urban and industrial marked areas.

Materials and methods

Origin of eggs: The eggs were collected and immediately frozen by members of the Peregrine Falcon Protection Association (AGW). After opening the eggs their content was homogenized and the fat was separated. In order to use the isotope dilution method, the 17 $^{13}C_{12}$-2,3,7,8-substituted PCDD/PCDF, 18 $^{13}C_{12}$-PCB (PCB-28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 165, 157, 167 169, 180, 189), and ε-HCH as the internal standard for the analysis of the chlorinated pesticides were added to the fat. By using a silica gel column loaded with sulphuric acid, the fat was removed. On a florisil column PCDD/PCDF were separated from PCB. The PCDD/PCDF-fraction was furthermore cleaned on Carbopack C/Celite 545, while the PCB-fraction was separated on Charcoal/ Chromosorb WHP into two sub-fractions, one containing the indicator- as well as the mono ortho-PCB and the other one containing the non-ortho PCB. Chlorinated pesticides were cleaned up separately by means on gel permeation chromatography and subsequent mini silica gel column chromatography.
The analytical measurements of PCDD/PCDF, and PCB were carried out by using capillary gas chromatography/high resolution mass spectrometry (HRGC/HRMS) on a Thermo Fisher DFS system (PCB: HT-8 column) and a Waters AutoSpec (PCDD/PCDF: DB-DXN column; PCB: HT-8 column), each at a resolution of R = 10,000. The chlorinated pesticides were determined on an GC-ECD equipped with a DB-17 column and a DB-5 column.

Results and discussion:

The PCDD/PCDF-results ranged from 6.3 to 937 pg WHO-TEQ_{1997}/g fat, and the PCB-results (sum of PCB 138, 153 and 180) from 0.14 to 108 mg/kg fat, while the maxima of the three PCB were found in different samples. The p,p'-DDE as the major metabolite of the observed chlorinated pesticides ranged from 0.08 to 50.4 mg/kg fat (Table 1). It became obvious that there were considerable differences in the burden of the eggs of eagle owls (*bubo bubo*) and of peregrine falcons (*falco peregrinus*) (Table 2). A slight decrease over the time range 2000 – 2009 could be observed (Figure 1). The regional distribution of these POPs and p,p'-DDE shows some differences in dependency whether the samples came from rural, from urban or from industrial marked areas (Figures 2-4).

Conclusion:

Peregrine falcons can have a life-period of nearly twenty years and hatchings have been seen until this age[1]. Their preferred preys are pigeons but they also chase all birds with a weight up to 500 g including migratory birds[2]. Despite of the prohibition of DDT since 1977 the concentration of the metabolite p,p'-DDE was 50.4 mg/kg fat in the highest contaminated sample. The mean of 97 samples over a period of 10 years (2000 - 2009) was 16.5 mg/kg fat, thus in the high mg/kg range. The long life-period and the possibility to chase birds from outside of Europe can be the reason for this high burden of p,p'-DDE. The high concentration of PCDD/F and PCB can not be declared completely.

Literature

1. Wegner, P.: Jahresbericht des AGW 2008, 23
2. Sömmer, P.: Die Ernährung des Berliner Wanderfalkenbrutpaares. Pica 16, 1989, 120–128

Table 1: PCDD/PCDF, PCB and p,p'-DDE in eggs of peregrine falcons from North Rhine Westphalia 2000 - 2009

Parameter	PCDD/F pg WHO-TEQ_{1997}/g fat	DL-PCB pg WHO-TEQ_{1997}/g fat	p,p' - DDE mg/kg fat	PCB#138 mg/kg fat	PCB#153 mg/kg fat	PCB#180 mg/kg fat
Minimum	6.3	117	0.08	0.05	0.06	0.03
Maximum	937	3583	50.4	31.4	44.0	36.9
Mean	188	1146	16.5	6.8	13.1	9.4
Median	158	957	14.5	5.1	11.3	7.6
90^{th} Perc.	336	2214	30.8	15.9	22.1	16.5
95^{th} Perc.	399	2531	38.1	18.4	31.2	25.8
n	103	53	97	97	97	97

Table 2: Comparison of PCDD/PCDF, PCB and p,p'-DDE in eggs of peregrine falcons and eagle owls mean 2000 - 2009

Parameter	n	PCDD/F pg WHO-TEQ_{1997}/g fat	DL-PCB pg WHO-TEQ_{1997}/g fat	p,p' - DDE mg/kg fat	Sum of PCB 138, 153, 180
peregrine falcon	103	176.1	1150	16.2	29.4
eagle owl	7	51.0	701	19.5	23,3

Figure 1: Development of PCCD/F-, p,p'-DDE- and sum of PCB-(138, 153, 180) results between 2000 and 2009

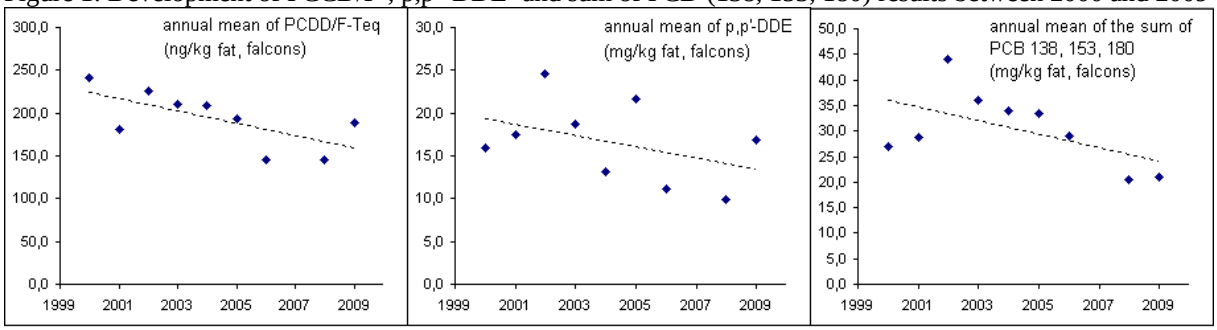

Figure 2: Regional distribution of p,p'-DDE in Nroth-Rhine Westfalia (mg/kg fat)

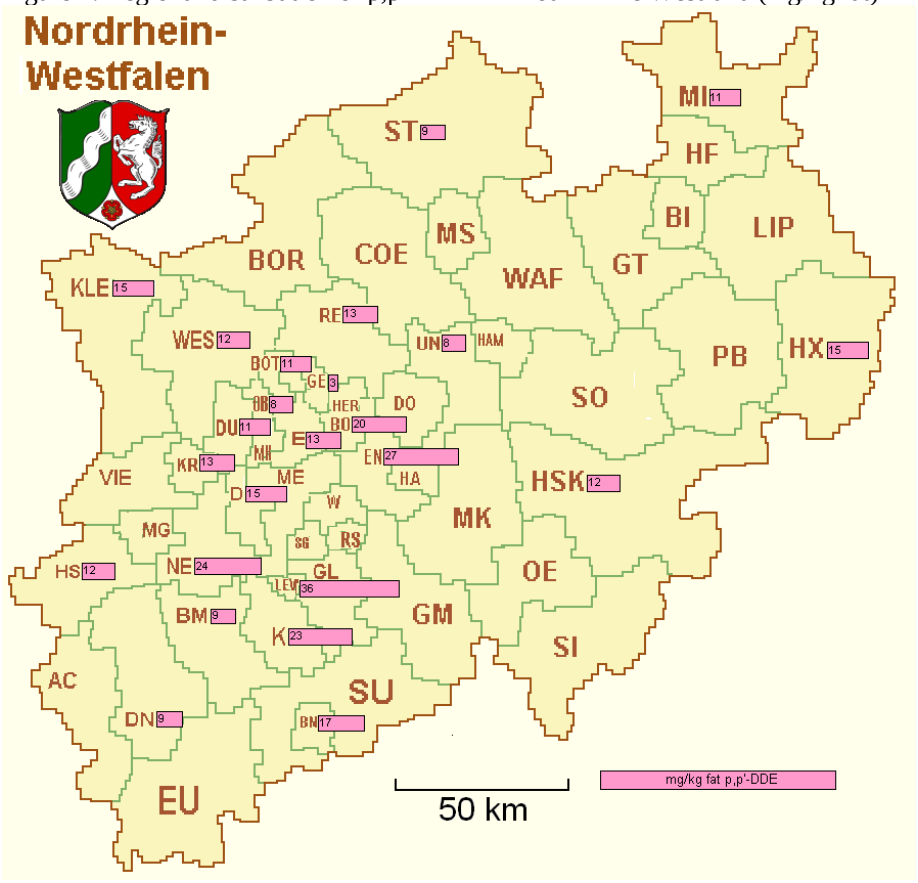

Figure 3: Regional distribution of PCB in Nroth-Rhine Westfalia (mg/kg fat; sum of PCB 138, 153, 180)

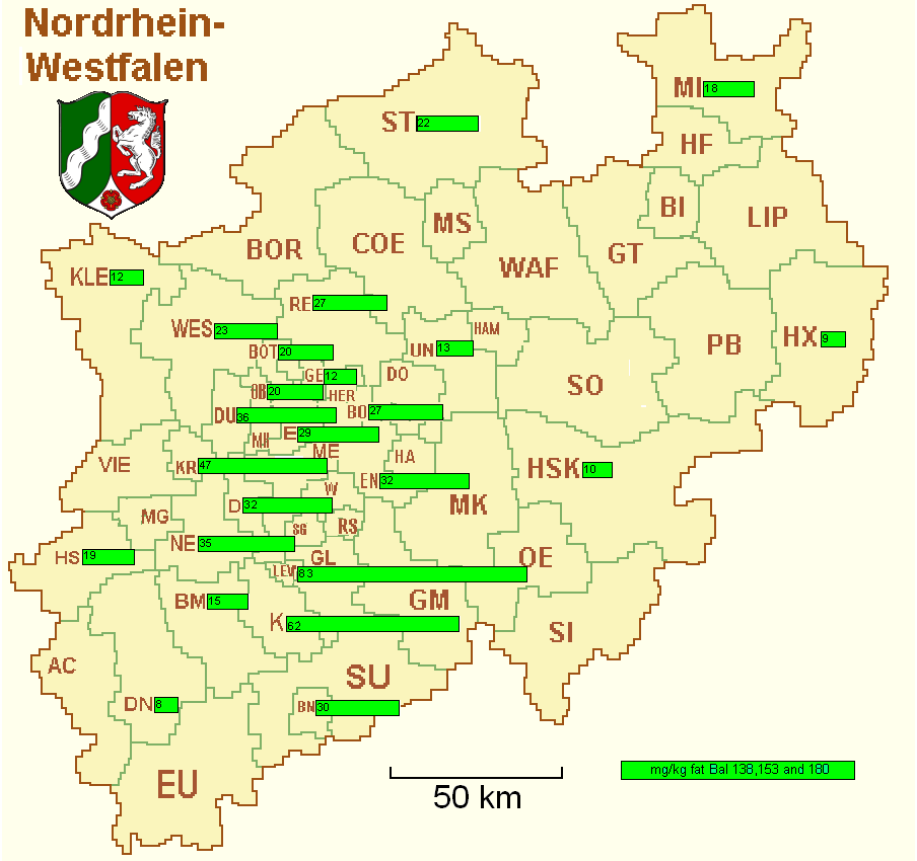

Figure 4: Regional distribution of PCDD/F in North-Rhine Westfalia (ng/kg fat PCDD/F-Teq (WHO 1997))