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# INFLUENCE OF CORMORANT GROUPINGS (*PHALACROCORAX CARBO* L.) ON CONTAMINATION OF THE ENVIRONMENT WITH ORGANOCHLORINE COMPOUNDS

Antoni Stefan Mikoszewski, Alicja Jabłońska

Institute of Zoology, University of Warsaw
Banacha str. 2, 02–097 Warszawa, mikst@biol.uw.edu.pl

**Summary.** Qualitative and quantitative analyses of organochlorine pesticides and quantitative analyses of polychlorinated biphenyls (PCBs) were performed for bottom sediments and plankton originating from three lakes where cormorant (*Phalacrocorax carbo* L.) groupings were recorded, that is, Lakes Inulec, Tuchlin and Czos, and for the purpose of comparison also from three lakes where groupings of those birds did not occur, that is Lakes Majcz Wielki Lake and Śniardwy (Łuknajno Bay) and the border zone between Lakes Mikołajki and Bełdany (ferry crossing in Wierzba). In samples from most of the lakes under study trace amounts of the following residual organochlorine insecticides and their metabolites were found: (1) in sediments: β-HCH, γ-HCH, 4,4'DDE, 4,4'DDD, 2,4'DDD, 2,4'DDT, (2) in plankton: γ-HCH, 4,4'DDE. No relationship was found between the occurrence of cormorant groupings and concentration of those substances, both in sediments and in plankton. Polychlorinated biphenyl (PCB) congeners were found in sediments originating from the three lakes where cormorant groupings were recorded and they were not found in sediments from the lakes used for comparisons. In plankton samples trace concentrations of PCB were recorded only for two lakes, namely, Tuchlin and Inulec. In most of the samples concentration of the compounds in question was not very high, however, it seems that cormorant groupings do contribute to environmental pollution with those compounds.

**Key words:** Mazurian Lakes, cormorant, polychlorinated biphenyls (PCBs), organochlorine insecticides

## INTRODUCTION

Organochlorine insecticides are characterised by high chemical stability, resistance to high temperature and strong acid and base activity, they are also lipophilic. Due to their carcinogenic and mutagenic effects they are harmful to various animal species, including humans [Biziuk 2001, Niemirycz *et al*. 2002].

Those compounds may reduce breeding success in birds due to decalcification of egg shells and toxic effects on embryos [Yamashita *et al*. 1993, Mason *et al*. 1997].

Polychlorinated biphenyls (PCBs) were manufactured to meet requirements of various industries because of their physical and chemical properties such as resistance to high temperature, low vapour pressure, relatively high flash points, low electrical conductivity and high thermal conductivity, chemical inertness, lipophilicity and low solubility in water. PCBs stability in the environment is related to the properties mentioned above. Most of the toxic effects of PCBs activity result from their long-term (so called chronic) impact on organisms. Those compounds cause, among others, nervous system disorders, reduce the level of A, B1 and B6 vitamins in the body, they are neurotoxic, affect mineral and hormone metabolism, weaken the immunological system, etc. [Birnbaum 1994, Falandysz 1999, Carpenter 2000, Freeman *et al*. 2000, Bast 2001, Faroon *et al*. 2001].

In spite of the fact that the use of organochlorine insecticides and PCBs has been discontinued in Poland over 20 years ago, they are still recorded in the environment, both in organisms and in its abiotic elements [Czaja 1996, Niewiadomska 1996, Bojanowska and Gliwicz 2005]. Also, animals are known to be capable of transporting pollutants, including the organochlorine compounds in question, from one habitat to another. Accumulated in animal fat tissue and organs, those pollutants may be transported from a place of their intake to distant locations and then released to the environment. Organochlorine compounds such as PCBs, DDT and its derivatives, HCH and its isomers, HCB, etc. are subject to bioaccumulation in the body and even low concentration at the initial levels of the food chain may increase (be biomagnified) in the bodies of animals representing higher trophic levels.

Being piscivorous species, the cormorant represents consumers at a high trophic level of the lake food chain. The food type and extensive feeding range of that species indicate that cormorants may accumulate organochlorine compounds at significant concentration in their organs and tissues, and then those substances are deposited in the environment in locations of that species groupings. Often, from a few tens up to several thousand individuals of the species may gather in such locations.

In this paper the authors analyse the processes of transporting and accumulating organochlorine compounds and the cormorant grouping contribution to the processes for selected Mazurian lakes.

## MATERIAL AND METHODS

Material for the analysis (42 samples of bottom sediments and 6 samples of plankton) were collected from the following three lakes of the Mazury Lakeland: Lakes Tuchlin, Inulec and Czos, where cormorant groupings had been reported for many years, and from three lakes where groupings of those birds were not found – Lakes Majcz Wielki, Śniardwy (Łuknajno Bay) and the border zone between Lakes Beładany and Mikołajki, hereinafter referred to as Wierzba after the name of the closest village. Plankton samples were collected from July 1st to July 10th , and sediments samples from September 14th to September 17th, 2007. Plankton was collected with a plankton net at the distance of some 10 m from a cormorant grouping (samples No. 4) and in lakes where cormorant groupings were not found, at the distance of 10 meters from the shore from which sediment samples were collected. Bottom sediments were collected with a „Czajka II" core probe, always the upper layer of sediments of 10 cm core height was taken.

Sediments were sampled in the lakes where cormorant groupings were found:

1 – from a reed field under a cormorant grouping,

2 – from a border zone between reeds and lake depths near a cormorant grouping,

3 – from a reed field at the opposite lakeshore,

Sediment samples were collected from the lakes used for comparisons:

A – from a reed field at the lakeshore,

B – from a border zone between reeds and lake depths.

In Wierzba, sediment samples were collected from a single location (A).

Extraction of residual organochlorine compounds from the collected material was performed after drying it completely. For plankton, all the obtained dry mass was analysed and bottom sediment samples weighted 10 grams. Extraction of residual organochlorine compounds from the material under study was performed as per methods recommended by the National Institute of Public Health [Ludwicki *et al.* 1996]. Organochlorine pesticides were extracted from appropriately prepared samples with hexane/acetone and after purification with sulphuric acid samples prepared for assaying were desulphurised with metallic copper. A UNICAM 60 gas chromatograph with an Electron Capture Detector (ECD) was used for qualitative-quantitative analysis of organochlorine pesticides. The reference standard was Supelco Pesticide mixtures Cat. No. 4–9151 containing the following substances: $\alpha$-HCH, $\gamma$-HCH, $\beta$HCH, heptachlor, aldrine, epoxidised heptachlor, 4,4'DDE, dieldrin, 2,4'DDD, endrin, 2,4'DDT,4,4'DDD, 4,4'DDT and hexachlorobenzene (HCB), code no. IPO LCI 290 from the Institute of Organic Chemistry.

Extraction of PCBs from the samples (averaged samples) was performed after concentrating the extract from assays of organochlorine pesticide residues to the volume of 1 ml. Then the samples were treated with a de-chlorinating reagent (2.5% solution of KOH in 96% $C_2$ $H_5OH$), heated in a water bath and then supplemented with $H_2O$ : $C_2H_5OH$ (1 : 1), and after evaporation the whole was treated with an oxidative reagent ($H_2O + H_2SO_4 + K_2Cr_2O_7$) and heated in a water bath at the temperature of. 90–100$^{o}$C for 30 min. After cooling the samples, the evaporated dissolvent was augmented to the volume of 1 ml, then 9 ml of distilled water was added and 2 $\mu$l samples for injection into a gas chromatograph were collected.

An UNICAM gas chromatograph, 610 series with ECD, was used for PCB assays in the material under analysis. For assays of organochlorine pesticide (HCB and PCB) residues in the analysed samples the chromatograph was equipped with a BPX 5 capillary column (non-polar phase) of 30 m length, mobile phase thickness of 0.25 μ, inner diameter of 0.22 mm and outer diameter of 0.33 mm.

Chromatograph specification:
injection chamber – 220°C, ECD – 320°C,
column oven – initial temperature 80°C for two minutes, then:
temperature increase 30°C/min up to 190°C,
temperature increase 6°C/min up to 280°C,
maintaining temperature of 280°C for 1 minute,
temperature increase 6°C/min up to 310°C,
maintaining temperature of 310°C for 10 minute.

Argon (Ar) was the carrier gas with quality certification, delivered by the Praxair company (argon contents 99.999 in volume %), dispensed with stream division under the pressure of 2.1 psi to the capillary column, division ratio 10 : 1. Volumes of hexane extracts and HCB standard, organochlorine pesticides and PCBs equalled 2 μl, as a result of gas stream division the volume of 0,2 μl reached the column. The PCBs reference standard was mixture of RPCM – 200 at the concentration of 2 ng/μl in isooctane by ULTRA SCIENTIFIC (USA), including PCB congeners 28, 52, 101, 118, 138, 153, and 180.

Extraction of organochlorine compounds from the study material and chromatographic analyses were performed at the Analytical Unit of the Department of Ecology, Institute of Zoology, University of Warsaw.

## RESULTS

### Organochlorine pesticides

In 23 out of 42 bottom sediment samples from various sample collection sites only trace residues (< 5ng $g^{-1}$) of organochlorine pesticides were found. In sediments from the lakes where cormorant groupings were recorded traces of the following pesticides were found:
Lake Czos – β-HCH, 4,4'DDE,
Lake Tuchlin – γ-HCH, 4,4'DDE, 2,4'DDT, 2,4'DDD.
No organochlorine pesticides were found in sediment samples from Lake Inulec.

In sediments from the lakes where cormorant groupings were not recorded, trace concentration of the following pesticides were found:
Lake Majcz Wielki – γ-HCH, 4,4'DDE,
Łuknajno Bay – γ-HCH, 4,4'DDE, 2,4'DDT, 2,4'DDD,
Wierzba – 4,4'DDE, 4,4'DDD.

The most often found compound at trace concentration was 4,4'DDE – it was identified in 15 out of 23 samples, and then γ-HCH which was found in 11 samples, β-HCH – detected in four samples, 2,4'DDT – found in 3 samples, 2,4'DDT – found in 2 samples, and 4,4'DDD – recorded in just one sample.

In plankton collected from the lakes, occurrence of the following compounds at trace concentration was confirmed: Lake Tuchlin – γ-HCH, Lake Inulec – γ-HCH, 4,4'DDE. In Wierzba – γ-HCH.

**Polychlorinated biphenyls (PCBs)**

Sixteen analyses of PCB residues in bottom sediments were performed. Occurrence of those compounds was recorded in 11 samples from the lakes where cormorant groupings were located. In contrast, they were not found in sediments of the lakes used for comparisons (Tab. 1). The highest PCB concentration was found in sediment samples from Lake Inulec: from 90 ng $g^{-1}$ in the

Table 1. PCBs (ng $g^{-1}$) in bottom sediments and plankton in lakes under study

| Lake | Area | Sediments | Area | Plankton |
|---|---|---|---|---|
| Tuchlin | 1<br>2<br>3 | 20<br>18<br>trace | 4 | trace |
| Czos | 1<br>2<br>3 | 40<br>40<br>15 | 4 | trace |
| Inulec | 1<br>2<br>3 | 90<br>75<br>15 | 4 | trace |
| Majcz Wielki | A<br>B | nd<br>nd | 4' | nd |
| Zatoka Łuk. | A<br>B | nd<br>nd | 4' | nd |
| Wierzba | A | nd | 4' | nd |

1 – location of a cormorant grouping, 2 – a border zone between reeds and a lake in the vicinity of a cormorant grouping, 3 – a reed field at the lakeshore opposite to a cormorant grouping, 4 – plankton samples collected at the distance of 10 m from a cormorant grouping, 4' – plankton samples collected at the distance of 10 m from a reed field/lake border zone; A – a reed field at the lakeshore, B – a border zone between reeds and a lake; nd – not detected, (trace < 10 ng $g^{-1}$)

sample from underneath the cormorant grouping, through 75 ng $g^{-1}$ in the sample from the border zone between reeds and the lake depths, to 15 ng $g^{-1}$ in the sample from the opposite lakeshore (Tab. 1). The second highest PCB residue concentration in the bottom sediments was found in Lake Czos. Both in the samples from underneath the cormorant grouping and from the border zone between reeds and the lake depths, PCBs concentration was 40 ng $g^{-1}$ and – in the sediment sample from the opposite lakeshore the concentration was 15 ng $g^{-1}$ (Tab. 1).

The lowest concentration of the analysed compounds was found in the samples collected from Lake Tuchlin, from 20 ng $g^{-1}$ in the sample from underneath the cormorant grouping, through 18 ng $g^{-1}$ in the sample from the border zone between reeds and the lake depths, to the trace concentration of 10 ng $g^{-1}$ in the sample from the opposite lakeshore (Tab. 1).

Presence of PCB residues at trace concentration in plankton (< 10 ng $g^{-1}$) was found only in the samples from Lakes Inulec and Tuchlin; in samples collected from other lakes those compounds were not detected (Tab. 1).

## DISCUSSION

Residues of organochlorine compounds, both pesticides and polychlorinated biphenyls (PCBs), in organs and tissues of fish-eating birds originating from various locations in the world have been recorded for years [Malcolm *et al*. 2003, Harris *et al*. 2005]. So far, in Poland, studies of such compound residues have not been carried out within the areas where groupings of piscivorous birds are recorded. Therefore, residues of organochlorine pesticides and PCBs in bottom sediments and plankton form Mazurian Lakes where cormorant (*Phalacrocorax carbo)* groupings occurred were analysed in this study.

In samples from most of the lakes under study, trace amounts (< 5 ng $g^{-1}$ ) of the following residual organochlorine pesticides and their metabolites were found: γ-HCH, β-HCH, 4,4'DDE, 4,4'DDD, 2,4'DDT, and 2,4'DDT. The study of bottom sediments originating from the lakes where cormorant groupings did not occur, carried out in 2003–2005, also identified organochlorine compounds, including HCH, 4,4'DDE,4,4' DDD [IEP, Bojanowska *et al*. 2006]. Concentrations of organochlorine pesticides and their metabolites obtained in the above study were similar to those in our study. Thus, one may believe that cormorant groupings have no significant impact on the occurrence of organochlorine pesticides and their metabolites in bottom sediments from the lakes under analysis.

Presence of PCB in bottom sediment samples – from trace concentrations (< 10 ng $g^{-1}$) to 90 ng $g^{-1}$ – was recorded only in the lakes where cormorant groupings did occur (Tab. 1). Those compounds were not found in sediments from the lakes used for comparison. In the study mentioned above, presence of PCBs at trace concentration was found in sediments from only two lakes, that is, Białe Włodawskie and Tarnowskie Duże. There were no cormorant groupings on those lakes. That indicates there might be a relationship between the existence of cormorant groupings and PCBs occurrence in bottom sediments. Cormorants can have feeding grounds at distances of up to 50 kilometres from their grouping locations [Przybysz 1997]. As a result of biomagnification and bioaccumulation processes, cormorants consuming food only slightly contaminated with residues of organochlorine compounds (PCBs) accumulate those substances at significant concentration in their bodies. In locations of their groupings, composed of from a few tens up to several thousand individuals, cormorants deposit a substantial part of the absorbed organochlorine compounds. Thus, they form small areas contaminated with those substances.

Papers dedicated to the impact of cormorant groupings on the scale of environment pollution with residues of organochlorine compounds are lacking. Those substances are assayed principally in the fat tissue, organs or eggs of piscivorous birds. The authors found considerable concentrations of the compounds in question in birds representing the highest levels of the food chain, in cormorant eggs PCBs concentration reached up to 14000 ng $g^{-1}$ [Yamashita *et al*. 1993, Somers *et al*. 1993, Mason *et al*. 1997, Fabczak *et al*. 2001, Malcolm *et al*. 2003, Harris *et al*. 2005].

Our study draws attention to the impact of piscivorous birds on transportation and spreading of organochlorine compounds in the environment. That is of particular importance in such regions as Mazury. At the same time one should bear in mind that various human industrial activities have definitely the greatest impact on the occurrence of those substances in the environment and their spreading. The results produced by our study form a basis for further investigations of issues related to contamination transport by animals, with special focus on piscivorous birds forming large groupings.

## SUMMARY

1. Organochlorine pesticides and their metabolites were found in samples from the lakes under study at trace concentrations.

2. The highest PCBs concentration in the analysed material was found in the closest vicinity of a cormorant colony, which means the birds play a significant role in the transport of those substances and contaminating certain areas of the environment with them.

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## WPŁYW ZGRUPOWAŃ KORMORANA CZARNEGO (*PHALACROCORAX CARBO* L.) NA SKAŻENIE ŚRODOWISKA ZWIĄZKAMI CHLOROORGANICZNYMI

**Streszczenie.** Wykonano analizy jakościowe i ilościowe pestycydów chloroorganicznych oraz analizy ilościowe polichlorowanych bifenyli (PCBs) w osadach dennych i planktonie pochodzącym z trzech jezior, na których znajdują się zgrupowania kormorana czarnego (*Phalacrocorax carbo* L.) – Inulec, Tuchlin i Czos, oraz dla porównania z trzech jezior, na których nie ma zgrupowań tych ptaków – Majcz Wielki, Śniardwy (Zatoka Łuknajno) i pogranicze jezior Mikołajskiego i Bełdany (przeprawa promowa w Wierzbie). W próbach z większości badanych jezior stwierdzono śladowe stężenia pozostałości następujących insektycydów chloroorganicznych i ich metabolitów: (1) w osadach: β-HCH, γ-HCH, 4,4'DDE, 4,4'DDD, 2,4'DDD, 2,4'DDT, (2) w planktonie: γ-HCH, 4,4'DDE. Nie wykazano zależności między obecnością zgrupowań kormorana czarnego a stężeniami tych związków zarówno w osadach, jak i w planktonie. Kongenery polichlorowanych bifenyli (PCBs) stwierdzono w osadach pochodzących z trzech jezior, na których znajdują się zgrupowania kormoranów, nie stwierdzono ich zaś w osadach z jezior użytych do porównań. W próbach planktonowych PCBs stwierdzono w stężeniach śladowych wyłącznie w dwóch jeziorach – Tuchlin i Inulec. W większości prób stężenia tych związków nie są bardzo wysokie, należy jednak sądzić, iż zgrupowania kormoranów czarnych mają wpływ na zanieczyszczenia środowiska tymi związkami.

**Słowa kluczowe:** jeziora mazurskie, kormoran czarny, polichlorowane bifenyle (PCBs), insektycydy chloroorganiczne