# CONCENTRATIONS AND CONGENER PROFILES OF PCBs AND PCDDs/PCDFs IN FAT AND LIVER TISSUES OF WILD DUCKS COLLECTED IN NEW YORK STATE

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## Introduction

Wild ducks often reside in areas where there is documented evidence of environmental pollution and consequently they can bioaccumulate persistent organochlorine compounds (POCs) such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Concentrations of PCDDs and PCDFs in biota are generally at least three orders of magnitude lower than PCB concentrations. The relative differences in concentrations of the compound types were apparent when carcasses of lesser scaup wintering on the Indiana Harbor Canal near industrialized areas of East Chicago were analyzed for PCBs and PCDDs/PCDFs [1]. The PCB concentrations ranged from a low of 0.72 µg/g wet wt. in an imature male collected in January 1994 to a high of 14 µg/g for an adult male collected in March 1994 compared to a range of of 35.9 to 291 pg/g wet wt. for PCDDs/PCDFs in the same groups of scaup. The present study was designed to determine the concentrations and congener profiles of PCBs and PCDDs/PCDFs in fat and liver tissues of four species of wild ducks, common mergansers (*Mergus merganser americanus*), gadwalls (*Anas strepera*), wood ducks (*Aix sponsa*)and mallards (*Anas platyrhynchos*). The Massena area of the St. Lawrence River was the primary location for sample collections in 1988/89 and 1994. It was previously shown by this laboratory that sediments near industrial outfalls in the area contained high concentrations of PCBs, PCDDs/PCDFs and polycyclic aromatic hydrocarbons (PAHs) [2]. Wood ducks were unavailable in the Massena area and were therefore collected in 1994 near Glens Falls on the Hudson River, an area which was subject to PCB contamination from capacitor refilling operations. Control mergansers, mallards and wood ducks were collected from uncontaminated locations in the Adirondack State Park.

## Methods and Materials

*Collection of ducks*

In the first collection common mergansers and mallards were captured in the Massena area as mature adults in the late hunting season (February, 1988 and 1989) and gadwalls as pre-flight juveniles on August 10, 1988. In the second collection pre-flight juveniles were collected in the Massena area and at the control sites from August 2 – 16,1994. Additional samples from the Hudson River were collected on October 10, 1994 during the early hunting season.

*Analytical Methods*

Tissue samples were spiked with a mixture of ten [U- $^{13}$C] 2,3,7,8-substituted PCDDs/PCDFs and extracted by high speed homogenization with 50/50 (v/v) methylene chloride/hexane in the presence of

sodium sulfate and silica gel. Lipids were removed by polymer film dialysis using cyclopentane as a solvent. Free fatty acids and other polar contaminants were removed from the extracts on a multiadsorbent column containing silica gel, KOH-treated silica gel and silica gel bonded with benzenesulfonic acid. After solvent exchange to nonane the extract was separated into a PCB/PCDD/PCDF fraction and a PAH fraction by silica gel (13-24 µm particle size) column chromatography. The PCB/PCDD/PCDF fraction was cleaned up using a computer-controled chromatography system consisting of acid alumina, carbon and acid alumina columns coupled in series. Separation of the PCBs fom the PCDDs/PCDFs occurred on the first alumina column. Additional separation of the non-ortho-/mono-ortho PCBs from the noncoplanar PCBs was accomplished with a porous graphitic carbon high performance liquid chromatography column. The PCDD/PCDF fractions were analyzed in the selective ion monitoring mode by capillary GC-low resolution MS using a 60m x 0.25mm i.d. DB5 column coupled to a Hewlett-Packard mass selective detector. The two most abundant ions in the molecular ion clusters for the native and $^{13}C$-labeled tetra to octa congener groups were monitored. The PCBs in samples from the 1988 collection were analyzed by packed column GC with electron capture (EC) detection and from the 1994 collection by capillary GC/EC [3].

**Results and Discussion**

The levels of PCBs in liver tissue from the ducks collected in 1994 are shown in Table 1. The contaminants were present in common mergansers, mallards and wood ducks collected from control sites at concentrations below those found in the same species collected from the industrial sites. No control sites were identified for gadwalls and therefore background PCB concentrations for this species could not be determined. At the St. Lawrence River sites all the collected ducks were pre-flight juveniles with the exception of one juvenile mallard which had just acquired some flight feathers. The highest PCB concentration was found in liver tissue from one of three common mergansers captured in a channel between two islands in the center of the river (PG site). The PCB concentrations in the other two mergansers were exceeded only by the PCB concentration found in the liver from a mallard collected near one of the aluminum smelters (RMC site) where there are sediments with high PCB concentrations [2]. The concentrations of PCBs in gadwalls collected at the same site and at a nearby upstream site (MGR site) and in a mallard collected near the second aluminum smelter (GRA site) were also elevated (258-498 ng/g). The lowest PCB concentrations were found in three mallards captured at a site in the center of the river downstream from the industrial plants (CI site). Similar relative differences between PCB concentrations in the liver samples were found when the results were expressed on a lipid or on a wet weight basis. These results show that the liver PCB concentrations were influenced by both species trophic level and sampling location. While the common mergansers were captured at a location which was remote from the industrial plants this species consumes fish and therefore is at a higher level on the food chain than the two dabbling duck species, gadwalls and mallards, which primarily consume aquatic vegetation. However the dabbling ducks do have the potential to bioaccumulate elevated PCB concentrations when they frequent contaminated areas. At the Hudson River site two wood ducks had X5 lower PCB levels than a mallard. The differences between the PCB levels in these two species can also be explained on a food chain basis since a large portion of an adult wood duck's diet consists of terrestrial vegetation, particularly acorns, and terrestrial vegetation is generally less contaminated than aquatic vegetation.

In contrast to the PCB results, at the St. Lawrence River sites the PCDF concentrations in liver samples from the five gadwall specimens and one mallard exceeded the PCDF concentrations in similar tissues from common mergansers. It is apparent from the data in Table 1 that the differences between the PCDF levels in the dabbling duck species and the common mergansers result from the presence of both 2,3,7,8-substituted and non-2,3,7,8-substituted isomers in the gadwall and mallard

tissues whereas the common mergansers were contaminated primarily with 2,3,7,8-substituted PCDF isomers. The absence of non-2,3,7,8-substituted isomers from the common merganser tissues can be explained by the combined effects of diet and metabolism. In general mammals [4] and aquatic vertebrates [5] metabolize PCDDs/PCDFs by hydroxylation of the lateral (2, 3, 7 and 8) positions which are not occupied by chlorine atoms. Consequently there is a selective retention of 2,3,7,8-substituted PCDDs/PCDFs. In the case of the common mergansers the PCDDs/PCDFs in their tissues have been subjected not only to internal metabolism but also to prior metabolism by those fish which constitute their diet. However there is no evidence that plant materials in the diet of gadwalls and mallards have the capability to metabolize PCDDs/PCDFs. Diet together with sampling location may explain why the common mergansers were the only species contaminated with PCDDs (10-51 pg/g total, all 2,3,7,8-substituted). Since the mergansers were collected in a channel between two islands in the middle of the St. Lawrence River some of the fish consumed by the ducks may have frequented the Canadian side of the river where there are several industries, including a pulp and paper mill, which could have released PCDDs into the environment. Also, as in the case of the PCBs, this part of the river may have received some input of PCDDs from Lake Ontario where there is substantial evidence of PCDD contamination in fish [6] and other biota. However PCDDs are present only as minor trace contaminants in sediments near the industrial outfalls on the US side of the St. Lawrence River whereas ng/g to µg/g quantities of PCDFs have been found in the same sediments. It is unlikely that the pre-flight gadwalls and mallards, collected near the shore on the US side, would have crossed through strong currents to the Canadian side, even when accompanied by adults.

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# LEVELS IN BIOTIC COMPARTMENTS

**Table 1.** Concentrations of total polychlorinated biphenyls (PCBs), coplanar PCBs and polychlorinated dibenzofurans (PCDFs) in liver tissue of ducks collected in 1994 in New York State from background sites (CT) and from contaminated sites on the the St. Lawrence (SLR) and Hudson Rivers (HR) (Species: CMG =Common Merganser, GAD =Gadwall and MAL = Mallard)

| | | PCBs (ng/g wet wt.) | | PCDFs (pg/g wet wt.) | | | |
|---|---|---|---|---|---|---|---|
| Species | Collection Site /Replicate No. | Total PCBs | Coplanar PCBs | 2,3,7,8- -TCDF | Total TCDFs | 2,3,7,8- -peCDFs | Total -peCDFs |
| CMG | CT-CL | 81 | 3 | 1.3 | ND | ND | ND |
| | SLR-PG#1 | 720 | 157 | 7.2 | 7.2 | 8.7 | 8.7 |
| | SLR-PG#2 | 930 | 155 | 16 | 17 | 6.2 | 7.1 |
| | SLR-PG#3 | 13800, 14600 | 1900, 1600 | 1.56, ND | 3.3, 1.8 | 74, 50 | 74, 50 |
| GAD | SLR-MGR#1 | 340 | 44 | 7.6 | 37 | 28 | 45 |
| | SLR-MGR#2 | 330 | 52 | 10 | 80 | 41 | 82 |
| | SLR-RMC | 258 | 46 | 11 | 79 | 35 | 63 |
| MAL | CT-PR#1 | 20 | 4 | 1.0 | 1.3 | ND | ND |
| | CT-PR#2 | 1.8 | 0.6 | ND | ND | ND | ND |
| | CT-PR#3 | 0.6 | NA | ND | ND | ND | ND |
| | SLR-RMC | 1920 | 535 | 18 | 160 | 59 | 150 |
| | SLR-CI#1 | 95 | NA | ND | ND | ND | ND |
| | SLR-CI#2 | 159 | NA | 1.4 | 6.5 | ND | ND |
| | SLR-CI#3 | 150 | 26 | 1.0 | 3.4 | ND | ND |
| | SLR-GRA | 405, 590 | 219, 101 | 3.4, 1.5 | 6.1, 2.4 | 2.3 | 2.3 |
| | HR-FE | 367 | 37 | 1.4 | 3.5 | ND | ND |