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# **Chemistry and Ecology**

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# **Polychlorinated biphenyl (PCB) residues in European roe deer (***Capreolus capreolus***) and red deer (***Cervus elaphus***) from north-western Poland**

Agnieszka Tomza-Marciniak <sup>a</sup> , Bogumiła Pilarczyk <sup>a</sup> , Marta Wieczorek-Dąbrowska  $^{\rm b}$  , Małgorzata Bąkowska  $^{\rm a}$  , Agata Witczak  $^{\rm c}$ 

& Diana Hendzel<sup>a</sup>

<sup>a</sup> Department of Animal Reproduction Biotechnology and Environmental Hygiene, West Pomeranian University of Technology in Szczecin, Poland

**b** National Research Institute of Animal Production, Research Station Kołbacz, Stare Czarnowo, Poland

c Department of Toxicology, West Pomeranian University of Technology in Szczecin, Poland

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# **Polychlorinated biphenyl (PCB) residues in European roe deer (***Capreolus capreolus***) and red deer (***Cervus elaphus***) from north-western Poland**

Agnieszka Tomza-Marciniak<sup>a\*</sup>, Bogumiła Pilarczyk<sup>a</sup>, Marta Wieczorek-Dąbrowska<sup>b</sup>, Małgorzata Bąkowska<sup>a</sup>, Agata Witczak<sup>c</sup> and Diana Hendzel<sup>a</sup>

*aDepartment of Animal Reproduction Biotechnology and Environmental Hygiene, West Pomeranian University of Technology in Szczecin, Poland;* <sup>*b</sup>National Research Institute of Animal Production,*</sup> *Research Station Kołbacz, Stare Czarnowo, Poland; cDepartment of Toxicology, West Pomeranian University of Technology in Szczecin, Poland*

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The purpose of this study was to evaluate polychlorinated biphenyls (PCBs) contamination levels in roe and red deer from north-western Poland and to assess environmental pollution in this area. A quantitative analysis was conducted using a capillary gas chromatography*/*mass spectrometry method. The mean concentrations of  $\Sigma$ PCBs (sum of PCBs: 28, 52, 101, 138, 153, 180) in liver samples were  $30.24 \pm 1.00$ 12.35 ng · g<sup>-1</sup> of lipid weight (l.w.) in roe deer and 60.13  $\pm$  14.23 ng · g<sup>-1</sup> l.w. in red deer, compared with  $24.21 \pm 10.02$  and  $45.22 \pm 9.77$  ng · g<sup>-1</sup> in the lungs of roe and red deer, respectively. PCBs 138, 153 and 180 were the dominant congeners in the liver samples of the analysed animals, whereas PCB 138 and 153 in the lungs. TEQs levels calculated for only dioxin-like PCBs were low: 0.32 and 0.29 pg WHO-PCB-TEQ · g<sup>-1</sup> fat in liver of red deer and roe deer, respectively. The mean PCB concentrations obtained in our study for organs of roe deer and red deer were several times lower than those reported elsewhere. These findings show that the investigated roe and red deer originated from an area with low levels of PCB contamination.

Keywords: polychlorinated compounds; indicator PCBs; dioxin-like PCBs; roe deer; red deer; liver; lung

### **1. Introduction**

Because of their physicochemical properties, polychlorinated biphenyls (PCBs), compounds of anthropogenic origin, have found widespread application in various branches of industry. Longterm mass production and broad application of PCBs, coupled with the long persistence of these compounds, has created favourable conditions for their accumulation in all parts of the environment [1–5]. PCBs have been released to the environment as a result of leakages, ashing, disposal of industrial effluents, waste storage and evaporation, and it has been estimated that ∼31% of annual PCB production has found its way into the environment [6].

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<sup>\*</sup>Corresponding author. Email: Agnieszka.Tomza-Marciniak@zut.edu.pl

494 *A. Tomza-Marciniak* et al.

Agricultural and forest soils are contaminated by PCBs mainly through atmospheric currents that move the co-distillates of these compounds over very large distances [7]. The transfer of organochlorine compounds from contaminated soil into plants and successive levels of the food chain poses a serious health risk for humans and animals. Previously published data suggest that despite a more than 30-year ban on the use of technical preparations containing PCBs, these compounds are still detectable in wildlife, foodstuffs and human milk [3,8].

The bioaccumulation of environmental pollutants is typically assessed by measuring these chemicals in the tissues of animals and humans. Research concerning the residues of organochlorine compounds in the tissues of wild animals has primarily focused more on birds, fish and marine mammals [9,10] and less on terrestrial mammals [3,11]. Because of their simple diet and small home range, free-living animals such as red and roe deer are useful indicators for monitoring the contamination level of terrestrial ecosystems (especially agricultural and forest lands) with compounds such as PCBs. Red deer are strongly associated with grassy areas within or adjacent to forest environments, whereas roe deer are able to inhabit both compact forest complexes and woodless areas. Both species feed on trees and bushes, which provide food in the form of shoots, bark, leaves and fruit, and on green plants and field crops.

To date, there has been no systematic analysis of samples taken from wild animals, which provide not only information on the level of environmental contamination, but also the potential toxicological threat to game consumers.

The aim of this study was to evaluate PCBs contamination levels in roe and red deer from north-western Poland and to assess environmental PCB pollution.

# **2. Materials and methods**

#### **2.1.** *Samples*

Samples (liver, lungs) originated from 25 roe deer (13 female and 12 male) and 24 red deer (10 female and 14 male) of various ages. The ages of roe and red deer were  $2.7 \pm 1.1$  years (female  $3.0 \pm 1.0$  and male  $2.3 \pm 1.1$  years) and  $2.1 \pm 0.8$  years (female  $2.1 \pm 0.7$  and male  $1.9 \pm 0.9$ years), respectively. Mean body weights of roe and red deer were  $17.8 \pm 2.8$  kg (female 19.1  $\pm$ 2.3 kg; male  $16.1 \pm 2.6$  kg) and  $91.9 \pm 26.2$  kg (female  $75.9 \pm 7.3$  kg; male  $104.9 \pm 29.5$  kg), respectively.

The animals were obtained from individual game shooting and from two wild game collection centres operating on the edge of Goleniowska Forest (Miedwie 53◦34 N, 14◦87 E and Maszewo 53°29′N, 15°03′E), in north-west Poland. Samples were collected in the autumn of 2007–2009. The liver and lungs were excised and homogenised from each animal. All samples were frozen (−20◦C) and stored in the laboratory until analysis.

## **2.2.** *Analytical determination*

Subsamples of 10–14 g were taken for analysis. Each sample was ground with anhydrous sodium sulfate (Chempur) in a mortar until a loose homogenous substance was obtained. The extraction of the dioxin-like PCB congeners (non-*ortho*: 77, 126, 169 and mono-*ortho*: 114, 118, 156, 157) and six indicator congeners (28, 52, 101, 138, 153 and 180) was carried out together with lipids in a Soxhlet apparatus (for 6 h) using a 150 mL mixture (v/v, 1:2.5) of *n*-hexane (Merck KGaA, Germany) and acetone (POCH, Poland). The obtained extracts were concentrated to  $\sim$ 2 mL in a rotary vacuum evaporator at 50◦C and transferred quantitatively with *n*-hexane to 10 mL dried and weighed test tubes with glass ground stoppers. To determine the lipids percentages, the dissolvent was evaporated under a stream of nitrogen  $(N_2)$ , and the residue was dried at 80 $°C$  to

a solid mass. After determining the masses of the lipids, the test tubes contents were dissolved in 2 mL of *n*-hexane and purified by adding 6 mL of sulfuric acid (Merck KGaA, Germany). After separation of the layers, the upper (*n*-hexane) layer was quantitatively transferred to a 10 mL test tube, washed three times with deionised water and dried over anhydrous sodium sulfate in a 8-mL LiChrolut® glass column. The dried extract was evaporated and transferred to a glass column packed with activated Florisil (Sigma Aldrich). The column was eluted with *n*-hexane. The obtained eluate was concentrated to 1 mL using dry nitrogen gas blowdown  $(N_2)$  and subjected to gas-liquid chromatographic separation using the method of capillary gas chromatography with mass spectrometry GC*/*MS. Chromatographic analyses were performed using the following chromatograph conditions: column temperature programme: 130◦C (hold 0.5 min), increase rate 7°C · min<sup>-1</sup>  $\rightarrow$  200°C (hold 5 min), increase rate 4°C · min<sup>-1</sup>  $\rightarrow$  280°C (hold 10 min), carrier gas: helium, flow rate 1.1 cm<sup>3</sup> · min<sup>-1</sup>, pressure 0.18 MPa (26.5 psi) and column: 60.0 m; ID  $250 \,\mu m$ ; film thickness  $0.25 \,\mu m$ .

PCBs were identified and quantified against three standard solutions (LGC Standards GmbH, Wesel, Germany). The analytical accuracy of analyses was verified using a certified reference material (ERM-BB445, LGC Standards GmbH, Wesel, Germany). The concentration of PCBs obtained in this study ranged between 72 and 96% of the reference values. For the calculation of means, samples with levels below the detection limit were assigned a value of one-half the detection limit. The limit of detection was  $0.02$  ng · g<sup>-1</sup>.

The concentration of six indicator PCB congeners was summed to obtain the  $\Sigma$ PCB. The toxic equivalents (TEQs) were calculated for dioxin-like PCBs (TEQ-PCB) using the toxic equivalency factor (TEF) values defined by WHO [12].

#### **2.3.** *Statistical data analyses*

Statistical analysis of the data was performed using Statistica software (Statsoft Inc., version 7.1 Statsoft). Prior to analyses data were investigated to determine their distribution using the Shapiro–Wilks' *W*-test. PCB concentrations between sexes, species and organs were compared by the Mann–Whitney *U*-test. Differences were considered as significant at the level of *p <* 0.05. Relationships between PCB concentrations in organs and the body weight and age of examined animals were evaluated by calculating the coefficients of correlation.

#### **3. Results**

The concentration of PCB congeners in the liver and lung samples from roe and red deer are given in Tables 1 and 2, respectively. The livers of the analysed animals were characterised by a higher concentrations of indicator PCBs than the lungs. The mean concentration of ΣPCBs (sum 6 of indicator congeners) in the liver was  $30.24 \pm 12.35$  ng · g<sup>-1</sup> of lipid weight (l.w.) in roe deer and 60.13  $\pm$  14.23 ng · g<sup>-1</sup> l.w. in red deer, compared with 24.21  $\pm$  10.02 ng · g<sup>-1</sup> l.w. in the lungs of roe deer and 45.22  $\pm$  9.77 ng · g<sup>-1</sup> l.w. in the lungs of red deer. Statistical analysis of these results showed that the observed differences in the ΣPCB concentrations between species in liver and lung were significant ( $p < 0.05$ ) (Table 3). In the male roe deer,  $\Sigma$ PCBs levels in liver and lung samples were higher than those in females, however, the differences were not significant  $(p = 0.816$  for liver and  $p = 0.542$  for lung).

It was observed that PCB 153 was the predominant congener in the organs of roe deer (10.99 ng · g<sup>-1</sup> for liver samples, 9.37 ng · g<sup>-1</sup> l.w. for lungs), and PCB 138 was the predominant congener in the organs of red deer (23.01 ng ·  $g^{-1}$  in the liver samples, 18.09 ng ·  $g^{-1}$  l.w. in lungs). The statistical comparison of values obtained for indicator congeners showed that levels of PCBs 138 and 153 in lungs and 138 in liver samples were significantly different between species (Table 3).

<b>PCB</b> <b>IUPAC</b> systematic	Liver			Lung			
numbering	All specimens	Female	Male	All specimens	Female	Male	
<b>Indicator PCB</b>	Concentration (ng $\cdot$ g <sup>-1</sup> lipids)						
2,4,4'-triCB (#28)	$3.22 \pm 1.43$	$3.41 \pm 1.01$	$3.13 \pm 1.34$	$3.44 \pm 1.72$	$3.57 \pm 1.22$	$3.28 \pm 1.15$	
$2,2',5,5'$ -tetraCB (#52)	$2.37 \pm 1.46$	$2.45 \pm 0.72$	$2.11 \pm 1.16$	$4.15 \pm 1.53$	$2.31 \pm 1.19$	$2.24 \pm 1.22$	
$2,2',4,5,5'$ -pentaCB (#101)	$0.98 \pm 0.60$	$0.89 \pm 0.53$	$1.32 \pm 0.68$	$1.30 \pm 0.55$	$1.33 \pm 0.87$	$1.45 \pm 0.74$	
$2,2',4,4',5,5'$ -hexaCB (#153)	$10.99 \pm 3.94$	$9.43 \pm 3.94$	$12.45 \pm 3.67$	$9.37 \pm 2.17$	$9.17 \pm 2.49$	$10.16 \pm 2.54$	
$2,2',3,4,4',5'$ -hexaCB (4138)	$6.57 \pm 1.36$	$4.18 \pm 1.17$	$8.19 \pm 2.18$	$6.99 \pm 3.31$	$5.89 \pm 1.38$	$8.25 \pm 2.24$	
2,2',3,4,4',5,5' hepta $CB$ (#180)	$6.09^{\rm A} \pm 1.78$	$5.11 \pm 2.55$	$7.58 \pm 2.14$	$2.87^{\rm A}$ + 1.56	$2.95 \pm 1.83$	$3.01 \pm 1.23$	
$\Sigma$ PCB		$30.24 \pm 12.35$ $25.45 \pm 11.12$	$33.27 \pm 13.04$	$24.21 \pm 10.02$	$23.57 \pm 9.13$	$26.49 \pm 8.51$	
Dioxin-like PCB	Concentration (pg $\cdot$ g <sup>-1</sup> lipids)						
$3,3',4,4'$ -tetraCB (#77)	$1.69 \pm 0.79$	$1.97 \pm 0.99$	$1.12 \pm 0.65$	$2.53 \pm 1.01$	$2.47 \pm 1.17$	$2.20 \pm 0.85$	
$3,3',4,4',5$ -pentaCB (4126)	$2.35 \pm 1.28$	$2.28 \pm 1.03$	$1.87 \pm 0.41$	$3.44 \pm 1.02$	$3.62 \pm 1.88$	$3.68 \pm 1.01$	
$3,3',4,4',5,5'$ -hexaCB (#169)	$2.78 \pm 1.32$	$3.01 \pm 0.78$	$1.78 \pm 0.81$	$2.97 \pm 1.33$	$3.72 + 2.26$	$2.83 \pm 1.20$	
2,3,4,4',5-pentaCB (H114)	$1.19 \pm 0.81$	$1.22 \pm 0.61$	$1.10 \pm 0.73$	$1.68 \pm 0.85$	$1.65 \pm 0.76$	$1.57 \pm 0.68$	
2,3',4,4',5-pentaCB (H118)	$3.55 \pm 1.32$	$3.23 \pm 1.78$	$3.89 \pm 2.82$	$2.30 \pm 0.98$	$2.38 \pm 1.29$	$2.29 \pm 0.53$	
$2,3,3',4,4',5$ -hexaCB (#156)	$1.43 \pm 0.65$	$1.47 \pm 0.90$	$1.29 \pm 0.58$	$2.19 \pm 1.24$	$2.22 \pm 1.57$	$2.14 \pm 0.55$	
$2,3,3',4,4',5'$ -hexaCB (H157)	$1.51 \pm 0.79$	$1.86 \pm 0.85$	$1.03 \pm 0.64$	$2.21 \pm 0.67$	$2.63^{\rm B} \pm 0.56$	$1.80^{\rm B} \pm 0.82$	
WHO-PCB-TEO	$0.29 \pm 0.10^{B}$	$0.32 \pm 0.09^C$	$0.21\pm0.04^\text{CD}$	$0.39 \pm 0.15^{\rm B}$	$0.38 \pm 0.18$	$0.40 \pm 0.13^D$	
Lipids $(\%)$	$2.05 \pm 0.60$	$1.86 \pm 0.57$	$2.42 \pm 0.71$	$1.74 \pm 0.70$	$1.39 \pm 0.65$	$1.47 \pm 0.90$	

Table 1. Concentration of selected polychlorinated biphenyl (PCB) congeners  $(\text{mean} \pm \text{SD})$  in the organs of roe deer from north-western Poland.

Note: A, B,..., the same letters denote statistically significant differences,  $p < 0.05$ .

Of the dioxin-like PCBs, the predominant congeners in the liver samples from roe deer were PCB 118  $(3.55 \pm 1.32 \text{ pg} \cdot \text{g}^{-1})$ , followed by PCB 169 and PCB 126. In lungs, the congeners with the highest concentrations were PCB 126 and PCB 169. The mean concentrations of PCB 126 in the liver and lungs of roe deer were  $2.35 \pm 1.28$  and  $3.44 \pm 1.02$  pg · g<sup>-1</sup>, respectively. PCB 118 was the predominant congener in liver and lung samples of red deer with mean concentrations of  $11.59 \pm 5.47$  and  $12.16 \pm 2.54$  pg · g<sup>-1</sup> l.w., respectively. Dioxin-like PCBs were ∼0.1% of the total concentration of the indicator PCBs.

The highest mean levels of WHO-PCB-TEQ were found in lungs of red and roe deer at 0.47 and 0.39 pg ·  $g^{-1}$  l.w., respectively (Tables 1 and 2). In roe deer, the differences in TEQ levels between females and males were observed, but only in liver of females WHO-PCB-TEQ was significantly  $(p < 0.05)$  higher  $(0.32 \text{ pg} \cdot \text{g}^{-1} \text{ l.w.})$  than in males  $(0.21 \text{ pg} \cdot \text{g}^{-1} \text{ l.w.})$ .

Roe deer lungs had a higher concentration of dioxin-like PCBs than the liver, although significant differences  $(p < 0.05)$  were not observed. Indicator PCB concentrations were highest in the liver and lungs of males, whereas dioxin-like PCB concentrations were highest in liver sample of females and in the lungs of males. However, these observed differences were not significant with the exception of PCB 157 in lungs ( $p = 0.005$ ). The content of indicator PCBs in red deer organs was about twice that of roe deer organs, whereas the levels of dioxin-like congeners were similar.

<b>PCB</b> <b>IUPAC</b> systematic	Liver			Lung		
numbering	All specimens	Female	Male	All specimens	Female	Male
<b>Indicator PCB</b>				Concentration (ng $\cdot$ g <sup>-1</sup> lipids)		
$2,4,4'$ -triCB (#28)	$2.40 \pm 1.20$	$2.62 \pm 1.28$	$2.17 \pm 1.10$	$2.35 \pm 0.97$	$2.49 \pm 0.92$	$1.93 \pm 0.63$
$2,2',5,5'$ -tetraCB (#52)	$1.05 \pm 0.51$	$0.87 \pm 0.49$	$1.02 \pm 0.41$	$1.11 \pm 0.59$	$1.26 \pm 0.60$	$0.97 \pm 0.41$
$2,2',4,5,5'$ -pentaCB (#101)	$1.98 \pm 0.98$	$1.99 \pm 1.02$	$2.00 \pm 0.83$	$2.12 \pm 0.72$	$1.32 \pm 0.65$	$2.88 \pm 0.96$
2,2',4,4',5,5'-hexaCB (4153)	$18.13 \pm 2.29$	$17.98 \pm 1.24$	$18.22 \pm 3.50$	$16.03 \pm 1.81$	$15.75 \pm 1.98$	$16.42 \pm 1.87$
2,2',3,4,4',5-hexaCB (4138)	$23.01 \pm 5.78$ $22.99 \pm 4.28$		$23.07 \pm 5.12$	$18.09 \pm 2.23$	$16.17 \pm 2.03$	$19.97 \pm 2.54$
$2,2',3,4,4',5,5'-$ hepta $CB$ (#180)	$10.52 \pm 2.01^{\rm A}$ $9.21 \pm 2.93$		$13.11 \pm 2.49$	$6.64 \pm 1.99$ <sup>A</sup>	$6.41 \pm 1.25$	$6.82 \pm 2.11$
$\Sigma$ PCB		$60.13 \pm 14.23$ 58.50 $\pm$ 11.27	$63.97 \pm 18.31$	$45.22 \pm 9.77$		$43.59 \pm 8.51$ $48.91 \pm 10.03$
Dioxin-like PCB				Concentration (pg $\cdot$ g <sup>-1</sup> lipids)		
3,3',4,4'-tetraCB (#77)	$1.59 \pm 0.67$	$1.23 \pm 0.92$	$1.82 \pm 0.91$	$2.31 \pm 1.22$	$2.37 \pm 1.34$	$1.98 \pm 0.99$
$3,3',4,4',5$ -pentaCB (#126)	$2.98 \pm 1.12$	$2.68 \pm 0.72$	$3.21 \pm 1.42$	$4.22 \pm 1.38$	$3.98 \pm 2.06$	$4.44 \pm 1.10$
$3,3',4,4',5,5'$ -hexaCB (#169)	$2.45 \pm 1.59$	$2.32 \pm 1.20$	$2.51 \pm 1.80$	$2.38 \pm 0.65$	$2.08 \pm 0.55$	$2.59 \pm 0.61$
$2,3,4,4',5$ -pentaCB (H114)	$3.71 \pm 2.42$	$3.32 \pm 2.54$	$3.94 \pm 2.27$	$5.15 \pm 1.20$	$4.77 \pm 1.23$	$5.38 \pm 1.17$
$2,3',4,4',5$ -pentaCB (#118)	$11.59 \pm 5.47$	$13.54 \pm 5.48$	$9.28 \pm 5.30$	$12.16 \pm 2.54$	$11.31 \pm 2.68$	$13.10 \pm 2.66$
$2,3,3',4,4',5$ -hexaCB (#156)	$1.54 \pm 0.73$	$1.69 \pm 1.03$	$1.33 \pm 0.10$	$1.40 \pm 0.92$	$1.63 \pm 1.20$	$1.33 \pm 0.86$
$2,3,3',4,4',5'$ -hexaCB (H157)	$1.28 \pm 0.81$	$1.33 \pm 0.92$	$1.20 \pm 0.71$	$1.46 \pm 1.32$	$2.17 \pm 0.94$	$0.74 \pm 1.36$
WHO-PCB-TEQ	$0.32 \pm 0.13$	$0.29 \pm 0.11$	$0.35 \pm 0.11$	$0.47 \pm 0.15$	$0.45 \pm 0.15$	$0.48 \pm 0.11$
Lipids $(\% )$	$1.72 \pm 0.63$	$1.50 \pm 0.67$	$2.03 \pm 0.81$	$1.46 \pm 0.68$	$1.57 \pm 0.87$	$1.43 \pm 0.44$

Table 2. Concentration of selected polychlorinated biphenyl (PCB) congeners in organs of red deer from north-western Poland.

Note: A, B..., the same letters denote statistically significant differences,  $p < 0.05$ .

Statistical analyses showed a positive but non-significant  $(p < 0.05)$  relationship between the concentration of indicator PCBs in the liver and the body weight and age of the analysed red deer. Of dioxin-like PCB congeners, only PCB 126 was positively correlated with the body weight of red deer and the correlation was statistically significant ( $r = 0.78$ ,  $p = 0.021$ ). This relationship was not observed for the organs of roe deer.

## **4. Discussion**

The degree of PCB accumulation in animal tissues is differs for each PCB congener due to differences in physicochemical properties, bioavailability, metabolism, half-life and biochemical processes that determine intake, distribution and elimination of xenobiotics. Safe [13] reported that among the various PCB congeners, PCB 138, PCB 153 and PCB 180 are considered to be the most abundant components in biological samples. Naso et al. [3] observed that PCBs were detected in 97% of the liver samples of roe deer from a protected area in the Emilia-Romagna region of northern Italy; PCBs 180, 153 and 138 were the most abundant congeners, accounting for ∼70% of total PCBs in the liver. Similar results were obtained in our study. Indicator PCBs were found in all liver samples and the proportion of dominant PCB congeners (PCBs 180, 153 and 138) in the

	$\boldsymbol{p}$							
		Roe deer			Red deer		Roe deer vs.	Roe deer vs.
	Male vs. Female			Male vs. Female				
<b>PCB</b> congeners	Lung	Liver	Liver vs. Lung	Lung	Liver	Liver vs. Lung	Red deer Lung	Red deer Liver
<b>Indicator PCB</b>								
<b>PCB 28</b>	0.324	0.389	0.357	0.138	0.425	0.754	0.357	0.680
<b>PCB 52</b>	0.236	0.187	0.173	0.152	0.189	0.682	0.137	0.236
<b>PCB 101</b>	0.425	0.138	0.236	0.324	0.489	0.542	0.425	0.173
<b>PCB 153</b>	0.285	0.682	0.094	0.109	0.236	0.425	$0.038*$	0.146
<b>PCB 138</b>	0.489	0.094	0.425	0.109	0.754	0.187	$0.027*$	$0.028*$
<b>PCB 180</b>	0.109	0.928	$0.011*$	0.094	0.094	0.542	0.109	0.137
$\Sigma$ PCB	0.542	0.816	0.173	0.425	0.137	0.187	$0.011*$	$0.032*$
Dioxin-like PCB								
<b>PCB 77</b>	0.425	0.187	0.357	0.236	0.173	0.324	0.187	0.094
<b>PCB 126</b>	0.783	0.094	0.109	0.425	0.542	0.138	0.173	0.425
<b>PCB 169</b>	0.146	0.137	0.720	0.489	0.824	0.542	0.285	0.146
<b>PCB 114</b>	0.285	0.236	0.680	0.236	0.285	0.236	0.680	0.137
<b>PCB 118</b>	0.138	0.680	0.189	0.542	0.146	0.324	0.236	0.824
<b>PCB 156</b>	0.720	0.425	0.754	0.783	0.189	0.720	0.236	0.754
<b>PCB 157</b>	$0.005*$	0.146	0.728	0.728	0.682	0.061	0.810	0.236
WHO-PCB-TEO	0.682	$0.045*$	$0.038*$	0.682	0.542	0.094	0.324	0.680

Table 3. Differences in polychlorinated biphenyl (PCB) concentration between sexes, organs and species (*p*-values).

∗Statistically significant differences at *p <* 0.05.

total weight of PCBs in the liver was 78.1% (20.1, 36.3 and 21.7%, respectively) (Figure 1). These congeners also had the highest concentration in the liver samples of red deer and their proportion of ΣPCBs exceeded 90.5% (31.8, 40.3 and 18.4% for PCBs 153, 138 and 180, respectively). Similar proportions of these compounds were observed in the lungs of analysed animals; PCB 138, PCB 153 and PCB 180 were the most dominant congeners, accounting for ∼70% of total PCBs in roe deer (24.9, 33.3 and 10.3%, respectively) and 88% in red deer (39.0, 34.6 and 14.3%, respectively) (Figure 1). Our findings corresponded with the results of other authors, who have studied PCB contamination levels in various terrestrial ecosystems [1,14,15]. Thomas et al. [4] suggested that the high concentration of hexa- and heptachlorobiphenyls is a consequence of their lipophilic properties and persistency, which is conducive to their bioaccumulation in soil and terrestrial ecosystems.

Many studies have shown that liver represents a depot organ for PCBs. Bachour et al. [1] observed that PCB 153 and PCB 180 preferentially accumulated in the liver of roe deer and foxes. Our study showed that the liver of the analysed animals was characterised by a higher concentrations of PCBs compared with the lungs. However, organ-specific differences were not significant  $(p < 0.05)$  for the tested PCBs (with the exception PCB 180 in roe deer).

The mean PCB concentrations obtained in our study for the liver samples from roe and red deer were several times lower than those reported elsewhere. Hernandez et al. [2] found that PCB concentrations averaged 137 ng ·  $g^{-1}$  l.w. in the livers of roe deer (Spain). Similar results (135.7 ng · g−<sup>1</sup> l.w.) were obtained by Naso et al. [3] in Italy. Much higher PCB levels in the liver (almost 500 ng · g−<sup>1</sup> l.w.) were obtained by Bachour et al. [1] for roe deer from Germany. In Poland, PCB levels in game animal tissues were investigated by Falandysz and Kannan [16], Szymczyk-Kobrzyñska and Zalewski [17] and Zasadowski et al. [18]. However, because adipose tissue was examined in these studies it is difficult to compare our results with the findings of these authors.



Figure 1. Percentage share of individual congeners in the sum indicator polychlorinated biphenyls in liver and lungs of roe and red deer from north-western Poland.

It is worth noting that in the organs of the animals studied (especially of roe deer), the highest concentrations among dioxin-like PCB congeners were characteristic of PCB 118 as well as PCBs 126 and 169, which are the most toxic congeners with a toxic equivalency factors of 0.1 and 0.01, respectively [12]. Likewise, Elkin and Bethke [15] observed that PCB 118 (in addition to PCBs 138, 153 and 180) dominated in the fat of caribou from Canada. However PCBs 126 and 169 were not detected, and they found PCB 77 only in several samples and at low levels. Much higher concentrations of PCB 118 and PCB 156, at over 40 and 20 ng · g<sup>-1</sup> lipids, respectively, were observed in livers of roe deer by Bachour et al. [1].

Many factors, such as the sex, age and season, influence the levels of PCBs [3,14,19]. We found that  $\Sigma$ PCB contents in the liver of female roe deer were lower than in males, and  $\Sigma$ PCB levels in lungs were higher in females than in males, however, these differences were not statistically significant.A significant difference in hepatic PCB levels between males and females was observed by Naso et al. [3], who explained that this situation may be due to the transfer of PCBs from mothers to offspring during pregnancy and lactation (i.e. an excretory route for PCBs). This mechanism is absent in male roe deer. Many authors have indicated that PCB bioaccumulation increases with the age of animals [14,19]. Although older animals (roe and red deer) were primarily characterised by higher PCB concentrations in our study, the observed correlation was not statistically significant  $(p = 0.188$  and 0.203).

The lower PCB concentration in the organs of the analysed animals compared with published data may be attributed not only to lower contamination of the environment inhabited by the animals, but also the shooting season. Naso et al. [3] indicated that in autumn animals accumulate lipid reserves, which they need to survive the critical period of winter and early spring.An increase in fat content (in organs and tissues) results in a reduction of the body's pollutant load.

Some researchers have indicated that lung is a target organ for the bioaccumulation of metabolically activated low-chlorinated PCB congeners [1]. Our study demonstrated that the proportions of PCB 180 (2,2',3,4,4',5,5'-heptachlorobiphenyl) in the lungs of roe and red deer were lower relative to the liver, in favour of the congeners with a smaller number of chlorine atoms per biphenyl molecule (especially PCB 52 and PCB 101). In roe and red deer, an approximately twofold lower fraction of PCB 180 in  $\Sigma$ PCB was observed in the lungs compared with the liver (Figure 1).

From a health safety point of view, it is important to determine the residues of PCBs (including dioxin-like PCB congeners) in animal raw materials and to evaluate the risk of consumer exposure. According to the European Union (UE) regulations, the maximum level for the sum of dioxins and dioxin-like PCBs (expressed as PCDD*/*F-PCB-TEQ) in the livers of terrestrial animals and products derived thereof is  $12 \text{ pg} \cdot \text{g}^{-1}$  fat [20]. In our study, TEQ levels calculated only for dioxin-like PCBs were 0.32 pg WHO-PCB-TEQ · g−<sup>1</sup> fat in livers of red deer and 0.29 pg WHO-PCB-TEQ ·  $g^{-1}$  fat in livers of roe deer. Suutari et al. [11] observed that the contributions of PCBs to total TEQs in reindeer and wild moose ranged from 34 to 68%. Relative to these proportions, we could state that the TEQs obtained here were low.

Our findings show that the investigated roe and red deer originated from an area with low PCB contamination, and the concentrations of the analysed compounds (lipid basis) in the livers of these animals were much lower than maximum levels considered acceptable by EU regulations.

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