SELECTIVE BIOACCUMULATION OF PCBs BY PHOCIDS FROM THE ESTUARY AND GULF OF ST. LAWRENCE

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Introduction

PCBs are ubiquitous in the environment and accumulate through the food web where elevated concentrations have been reported in high trophic level marine mammals (1). Some PCB congeners, however, show relatively low bioaccumulation potential because they are either less available from food, more easily metabolised or excreted by marine mammals. As a result, PCB patterns in these animals are generally less complex, showing fewer congeners than in their prey (2). PCB patterns in marine mammals may vary within and between species because of difference in their diet, sex, age and condition. In addition, the capacity of these animals to metabolise PCB congeners appears to be a key factor in defining their PCB patterns. A pharmacokinetic model was devised to assess the capacity of marine mammals to metabolize PCBs (3, 4). In this model, differences in PCB patterns between mammals and their prey are explained in terms of the biotransformation of individual PCB congeners as it relates to their structural characteristics. A recent application of the model to fish-eating mammals from northern Europe indicated that different mammalian species exhibit different abilities to metabolize PCBs (5). In the present study, the selective bioaccumulation of PCBs found in four seal species inhabiting the Estuary and Gulf of St. Lawrence was investigated by comparing their PCB patterns to those representative of their diet. Differences in PCB patterns were interpreted using the pharmacokinetic model devised by Boon et al. (4) for the biotransformation of PCBs in marine mammals.

Materials and Methods

Samples. Blubber samples were obtained from four different seal species sampled in the Estuary and Gulf of St. Lawrence. Harp seals (*Phoca groenlandica,* n=11) and hooded seals (*Cystophora cristata*, n=12) were captured near the Magdalen Islands in the centre of the Gulf of St. Lawrence. Grey seals (*Halichoerus grypus,* n=9) were sampled from the southern part of the Gulf near Port Hood and Amet Island, whereas harbour seals (*Phoca vitulina,* n=5) were captured in the western region of the St. Lawrence Estuary. Samples were obtained from either shot or live captured adult male seals. In the latter case, two blubber samples were taken from each animal using a biopsy punch. Whenever possible, blubber samples were taken at 60-70% of body length from the nose, approximately midway between the spinal column and the mid-lateral region of the mammal. Blubber samples extended the entire depth of the blubber layer. They were wrapped in solvent rinsed aluminum foil, placed in a sealed plastic bag and stored at –20°C.

Analysis of PCBs. Each skin free blubber sample (0.5-1 g wet wt) was chemically dried with sodium sulphate and then transferred to a glass column. A mixture of five $^{13}C_{12}$ PCBs was also added to the column before the lipids and lipophilic compounds were extracted from the sample with dichloromethane-hexane (50:50). Lipids were removed from the rest of the extract by gel

permeation chromatography. The extract was further cleaned by elution through a multi-layer column packed with acidic, neutral and basic silica or a two-layer column packed with neutral silica and alumina. The final extract was reduced in volume and spiked with an instrument performance solution containing two additional $^{13}C_{12}$ PCBs. Quantification of 22 PCBs (Table 1) was performed using a Varian 3400CX series gas chromatograph equipped with a Varian's Saturn II ion trap, a Varian 1078 split/splitless programmable injector (5 µl injection volume) operated in splitless mode, and a Varian 8200CX autosampler. Chromatographic separation of the contaminants was achieved using a 30m DB-5MS column (0.25 mm ID, 0.25 µm film thickness) with helium (He) as the carrier gas. The ion source was operated in electron impact (EI) ionisation mode and the ion trap in MS/MS mode. Concentrations of PCB congeners were calculated using relative response factors (RRFs) determined from a four point calibration curve. Precision and accuracy of PBC analysis were assessed by repeated analysis of the whale blubber SRM1945.

Calculation of PCB patterns. Normalised PCB patterns of individual seals, $R_{153}(PCB_x)$, were calculated by dividing the concentration of each PCB by the concentration of PCB 153, chosen as reference congener because of its high resistance to biotransformation and its prominence in all samples.

$$R_{153}(PCB_x) = \frac{[PCB_x]}{[PCB_{153}]}$$

Normalised PCB patterns of individual Atlantic cod (*Gadus morhua*) sampled in the Saguenay Fjord, the Estuary and the Gulf of St. Lawrence were also calculated. PCB data of Atlantic cod were available for 12 muscle and 12 liver samples (6).

Comparison of PCB patterns between seals and Atlantic cod. Normalised PCB patterns were compared between individual seals and individual Atlantic cod samples by calculating relative ratios $R_{rel}(PCB_x)$ for individual BPC congeners,

$$R_{rel}(PCB_x) = \frac{R_{153}(seal_i)}{R_{153}(cod_j)}$$

where $R_{153}(seal_i)$ represents the normalised PCB pattern of seal *i* and $R_{153}(cod_j)$ represents the normalised PCB pattern of cod sample *j*.

Results and Discussion

Results of relative ratios R_{rel} of PCB congeners found in the four seal species investigated compared to Atlantic cod are presented in box and whisker plots (Figure 1). For each species, R_{rel} were calculated for individual seals in relation to individual Atlantic cod samples. Atlantic cod was used as model food item because it constitutes at least a part of the diet of each seal species (8). Futhermore, using normalised patterns (R_{153}) from each individual fish samples in the calculation of R_{rel}, instead of average PCB patterns from all fish samples, was considered to be more representative of the variability of PCB patterns available to seals through their diet. PCB congeners measured in seal and fish samples were assigned to one of the five metabolic groups according to their structural characteristics and resistance towards biotransformation (Table 1). On each plot, PCB congeners were ordered from groups I to V and a vertical line was drawn to split congeners of groups I and II from groups III, IV and V (Figure 1). For each seal species examined, PCB congeners belonging to groups I and II show values of R_{rel} around unity. These results are in

agreement with those of reported by Boon et al. (5) indicating that PCBs belonging to groups I and II resist metabolic transformation by marine mammals. It has been shown, however, that PCB congeners from groups III, IV and V were metabolized by phocids but were generally less biotransformed by other marine mammals such as cetaceans (5, 9). In the present study, PCB congeners from groups III, IV and V show R_{rel} values lower than one in all seal species examined.

Table 1. Structural characteristics of PCB congeners and their assignment to the different metabolic groups[a]

Metabolic group	Structural characteristics of PCB congener	PCB congener[b]
I	congeners without any vicinal hydrogen (H)-atoms	153, 180, 187, 206, 209
II	congeners with vicinal H-atoms exclusively in the *ortho* and *meta* positions in combination with ≥ 2 *ortho*-Cl	99, 128, 138, 170
III	congeners with vicinal H-atoms in *ortho* and *meta* positions in combination with 1 *ortho*-Cl	28/31, 66/70, 74, 105, 118
IV	congeners with vicinal H-atoms in *meta* and *para* positions in combination with 2 *ortho*-Cl	44, 52, 87, 101, 110
V	congeners with vicinal H-atoms in the *meta* and *para* positions in combination with ≥ 3 *ortho*-Cl	149

a PCB congeners assigned to structural groups with regards to biotransformation (4)
b Numbering PCBs according to Ballschmiter and Zell (7)

In harbour seals, however, R_{rel} values for these less persistent PCB congeners were more variable than in the other phocids. The R_{rel} values for harbour and grey seals from the Estuary and Gulf of St. Lawrence are in good agreement with the results reported by Boon et al. (5) for the same species sampled in the northern Europe. Thus, the pharmacokinetic model applied by Boon et al. (5) to Northern European marine mammals also appears to be applicable to phocids from the Northeastern Atlantic. A preliminary interpretation of the results suggests that the four seal species investigated possessed similar abilities to bioaccumulate PCB congeners from groups I and II and to metabolize PCB congeners from groups III, IV and V (Figure 1). A thorough assessment of the abilities of these seal species to selectively bioaccumulate PCB congeners would require the consideration of the various food items included in their diet.

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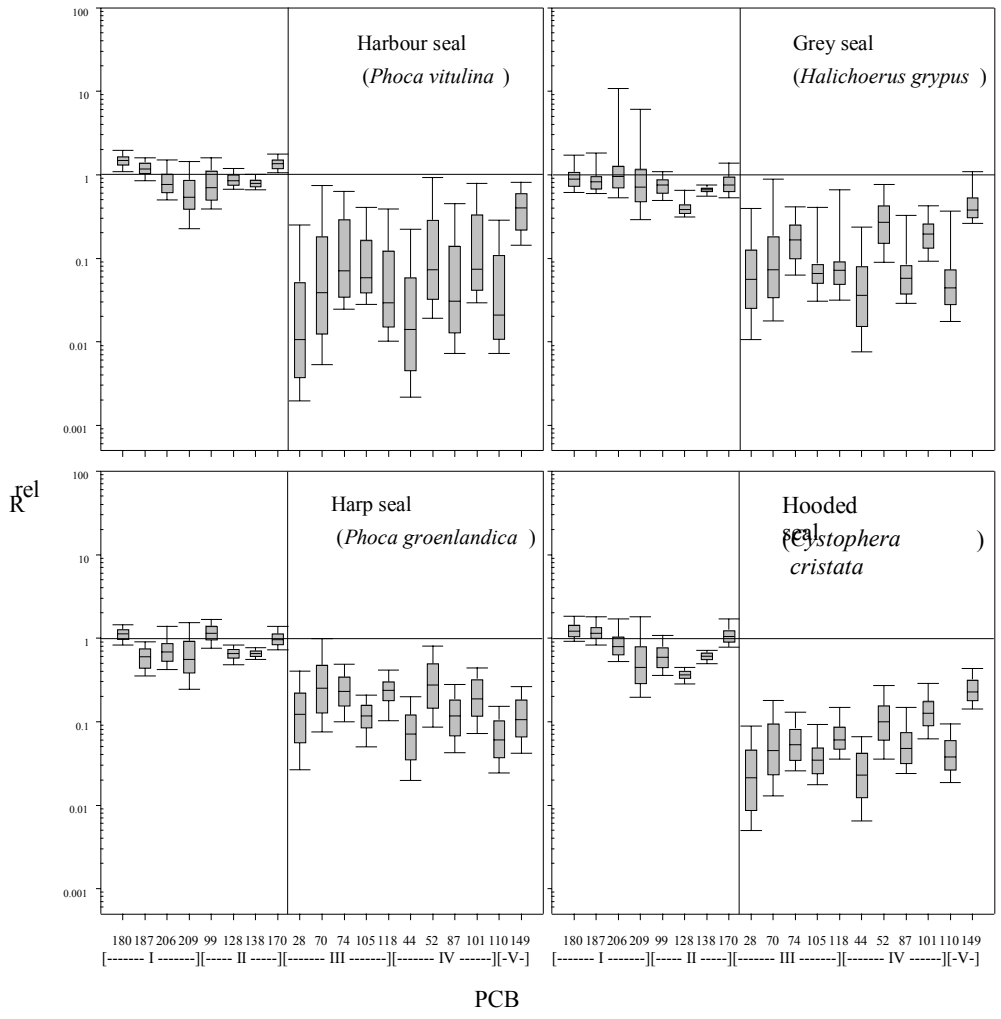

F**igure 1**. Box and whisker plots of the relative ratios (R_{rel}) of different PCB congeners in the four seal species investigated to the Atlantic cod (*Gadus morhua*) used as model food source. The central line of the box marks the median, and the upper and lower boundaries represent 75th and 25th percentiles, respectively. Whiskers above and below the box indicate 90th and 10th percentiles. PCB congeners 28 and 70 represent 28/31 and 66/70, respectively.

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