

# Polychlorinated camphenes (toxaphenes), polybrominated diphenylethers and other halogenated organic pollutants in glaucous gull (*Larus hyperboreus*) from Svalbard and Bjørnøya (Bear Island)

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**“Capsule”:** PCBs and *p,p'*-DDE constituted 90% of contaminants found.

## Abstract

The levels of polychlorinated camphenes (toxaphenes) were investigated in liver samples from 18 glaucous gulls (*Larus hyperboreus*) from Bjørnøya (74°N, 19°E) and four individuals from Longyearbyen (78°N, 15°E). Additionally brominated flame retardants (BFRs), PCBs and chlorinated pesticides were investigated in liver and intestinal contents of 15 of the glaucous gulls from Bjørnøya. Of the analysed BFRs only 2,2',4,4'-tetra- and 2,2',4,4',5-pentabrominated diphenylethers (PBDE 47 and 99) could be detected. The concentrations ranged between 2 and 25 ng/g ww. In addition, high resolution measurements with GC/HRMS revealed the existence of several, not quantified, PBDEs and polybrominated biphenyls (PBBs) congeners in the samples. B9-1679 and B8-1413 were the dominating toxaphenes with median concentrations of 8 and 15 ng/g ww. Concentrations of toxaphenes and PBDEs were up to 100-times lower than the concentrations of PCB and some of the pesticides. PCB and *p,p'*-DDE constituted 90% of the contaminants found. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Glaucous gull; Arctic; Brominated flame retardants; Toxaphenes; Persistent organic pollutants

## 1. Introduction

The variety of organic contaminants, released by the industrial part of the world, is a long-term threat to the remote Arctic environment (Burkow and Kallenborn, 2000; Muir et al., 1999). Besides conventional organic pollutants, such as polychlorinated biphenyls (PCBs) and chlorinated pesticides, several other compounds, such as polychlorinated camphenes (toxaphenes) and brominated flame retardants (BFRs), have been identified in Arctic biota (Sellström et al., 1993; Pijnenburg et al., 1995; Alaei et al., 1999; Tittlemier et al., 1999; Stern et al., 2000). Due to long range transport several of these compounds and their degradation products can reach remote Arctic areas. As a result of persistency and lipophilicity, these compound groups are able to bioaccumulate in food webs.

Toxaphene consists of a complex mixture of several hundreds of bornanes, bornenes, bornadiens and camphenes. Toxaphene was used as a pesticide worldwide until 1993. The total production was estimated to 1.3 million metric tons from the early 1950s until 1993 (Voldner and Li, 1993, 1995). Toxaphene was originally regarded as easily degradable. However, the most persistent components of the technical toxaphene mixture have been found in soil, water and sediment more than 10 years after use. Therefore, toxaphene is now regarded as ubiquitous and persistent. Toxaphene has not been used in Norway, but still high levels have been detected in biota from the Svalbard area. In some Arctic marine mammal samples, i.e. in harp seal blubber from the Barents Sea, the toxaphene levels exceed those of PCB (de Geus et al., 1999; Wolkers et al., 2000).

Polybrominated diphenyl ethers (PBDEs) belong to the group of additive BFRs, which are widely used in electronic equipment, insulation material and furniture. In 1998 the average yearly production of BFRs

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exceeded 150,000 tons (Larsen et al., 1999). The findings of BFRs in air and biological samples, collected in remote areas of the Arctic, indicate a worldwide distribution (Alaee et al., 1999; Jansson et al., 1987, 1993; Stern et al., 2000). Recent findings of increased levels of PBDEs in marine biota and human samples, prove the importance of further investigations of these compounds (Lindström et al., 1997; Meneses et al., 1999; Norén and Meironyté, 2000; Sjödin et al., 1999; Stanley et al., 1991). Because of the molecular analogies between PCBs and PBDEs, a comparable ecological and toxicological behaviour may be expected.

Bjørnøya is an important breeding site for glaucous gulls (*Larus hyperboreus*) inhabiting the Barents Sea (Mehlum and Daelemans, 1995). A total of 2000 pairs breed on Bjørnøya. The glaucous gull is a food-generalist, belonging to the scavenger-predatory species (Lydersen et al., 1989; Barry and Barry, 1990). Important components in the diet of glaucous gulls are eggs and chicks of other seabirds, fish, crabs, amphipods, but also seal blubber and garbage (Savinova et al., 1995; Henriksen et al., 2000).

The glaucous gull population inhabiting the Svalbard archipelago has been thoroughly investigated during the last decade with respect to their burden of PCBs and selected pesticides (Gabrielsen et al., 1995; Sagerup et al., 2000; Bustnes et al., 2001). This research was initiated by the finding of highly contaminated dead and sick gulls on Bjørnøya during the summer of 1989 (Gabrielsen et al., 1995). Further research was carried out on seemingly healthy gulls from Svalbard, Iceland and Greenland, in order to understand POP accumulation and possible effects on glaucous gulls. Also in these studies high levels of the conventional persistent organic pollutants (POPs), such as PCBs and chlorinated pesticides, were found in the glaucous gulls (Savinova et al., 1995; Borgå et al., 2001; Cleemann et al., 2000; Henriksen et al., 2000).

The objective of the present study was to investigate the contamination of toxaphenes and BFRs in relation to those of PCBs and chlorinated pesticides in glaucous gulls from Bjørnøya. To our knowledge, no information

exists about levels of toxaphene and BFRs in seabirds from this part of the Arctic.

## 2. Materials and methods

### 2.1. Sampling

Glaucous gulls were sampled at two different locations within the Svalbard archipelago in spring 1995. Three birds were shot at Bjørnøya (74°N, 19°E) whereas four birds were shot close to Longyearbyen (78°N, 15°E). All seven samples were collected between the middle of May and the beginning of June. Fifteen additional glaucous gulls were shot near Kapp Harry on the southwest coast of Bjørnøya just after the hatching period in July 1999. Liver and intestinal contents were chosen for analysis in order to study the relation between contamination in metabolising tissue and digested food items. The liver tissue represents the metabolising organ that the organohalogenes have to pass after uptake from the intestine, while the content in the lower part of the intestines represents the digested food.

After the birds were sacrificed, they were weighed by wing a Pesola spring balance to the nearest 10 grams. Morphological measurements, including skull length, bill height and depth and wing length, were taken by using a slide calliper and a ruler. Sex was determined by size, males being larger than females (Cramp and Simmons, 1983). We assumed that birds with a combination of a bill longer than 61.5 mm and skull length (head + bill-length) longer than 142 mm were males (Table 1). Whole liver samples were collected from all birds immediately after sacrifice. The liver samples were weighed to the nearest gram on an electronic balance, wrapped in aluminium foil and frozen at –20 °C. The samples were kept frozen until analysis. From the 15 birds collected in 1999, also intestines and stomach samples were taken. The gastro-intestinal system was removed, wrapped in aluminium foil and frozen at –20 °C. In the laboratory, the intestines were opened

Table 1  
Biometric data for glaucous gulls including analysed compound groups

| Sampling area | Sampling time | Number of samples | Average body weight (g) | Sex                          | Average lipid % in liver | Analysed compound groups                             |
|---------------|---------------|-------------------|-------------------------|------------------------------|--------------------------|--|
| Bjørnøya      | June 1995     | 3                 | 1900                    | 3 males                      | 8.1                      | Toxaphenes (7.0–9.2)                                 |
| Bjørnøya      | July 1999     | 15                | 1667                    | 7 males (1)<br>8 females (1) | 5.9                      | Toxaphenes, BFRs, PCBs, Pesticides incl. metabolites |
| Longyearbyen  | May 1995      | 4                 | 1757                    | 3 males<br>1 female          | 7.0                      | Toxaphenes   |

BFRs: brominated flame retardants; PCBs: polychlorinated biphenyls; (n) number of individuals with uncertain sex determination.

and the lower colon contents were removed for chemical analysis. The intestinal contents from all collected birds were pooled in order to obtain sufficient material for analysis. The stomachs were opened and the undigested food items were identified.

## 2.2. Analytical procedure

The liver samples collected in Longyearbyen and on Bjørnøya in 1995 were only analysed for toxaphene levels. The 15 liver samples and the pooled intestinal contents sample collected on Bjørnøya in 1999 were analysed for 18 chlorinated pesticides, including *p,p'*- and *o,p'*-dichlorodiphenyl-trichlorethane (DDT and its metabolites), 10 toxaphenes (B7–515, B8–786, B8–789, B8–1413, B8–1414, B8–2229, B9–915, B9–1025, B9–1679, B10–1110), 35 chlorinated biphenyls (PCBs) and several BFRs, such as 2,2',4,4'-tetrabromodiphenylether (PBDE 47), 2,2',4,4',5-pentabromodiphenylether (PBDE 99), 4,4'-dibromobiphenyl (PBB 15), 2,2',4,5'- and 2,2', 5,5'-tetrabromobiphenyl (PBB 49 and 52), 2,2',4,5,5'-pentabromobiphenyl (PBB 101) and 2,2',4,4',5,5'-hexabromobiphenyl (PBB 153), as well as hexabromobenzene, 2,4,6-tribromophenylallylether and hexabromocyclododecane. For quantification of all compounds, crystalline reference material was obtained from Promochem (Wesel, Germany). As internal standards <sup>13</sup>C-isotope labelled PCB 77, 118, 141 and 178 were used. All <sup>13</sup>C-isotope labelled internal standards were purchased from Cambridge Isotope Laboratories (Woburn, MA, USA). Solvents of pesticide grade were employed (E. Merck, Darmstadt, Germany).

Samples, consisting of 3–4.5 g frozen liver or pooled intestinal contents, were homogenized with a 10-fold amount of pretreated sodium sulfate (600 °C for 8 h). The homogenate was fitted in a glass column and extracted three times using 50 ml cyclohexane/acetone (3:1; v/v), 60 minutes each time. The amount of extractable lipid was determined gravimetrically.

The main lipid removal step was performed on a gel permeation system consisting of a dual prepacked Waters Envirogel system (Bio beads SX3 resins, 37–75 µm id; column 1: 19 mm id, 150 mm length; column 2: 19 mm id, 300 mm length) with cyclohexane/ethyl acetate (1:1; v/v) at a flow rate of 5 ml/min. Remaining lipids were removed by using a glass column system (13 mm id, 1090 mm length) purchased from LATEK (Eppelheim, Germany) and packed in our laboratory with 50 g Biobeads S-X3 (Biorad, Hercules, CA, USA). A flow rate of 1 ml/min of cyclohexane/ethyl acetate (1:1; v/v) was applied. An additional fractionation was carried out on a silica column (2 g pretreated silica purchased from Merck; particle size 0.063–0.2 mm, heated for 8 h at 600 °C and deactivated with 1.5% w/w water). The column was eluted with: (1):25 ml *n*-hexane/toluene (60:35; v/v) and (2):30 ml *n*-hexane/toluene

(50:50; v/v) containing all POPs of interest. Fractions 1 and 2 were combined and reduced to 200 µl. All samples were prepared in parallel. To cover blind contamination, a double set of method blanks was run for each sample set.

A CE Instruments 8560 Mega gas chromatograph (Milan, Italy) was equipped with a 30m JW DB5-MS (0.25 mm id and 0.25 µm film thickness). Helium (He, 5.0 quality) was used as carrier gas at a flow rate of 1 ml/min. Temperature program: 60 °C, 2 min, 15 °C/min to 180 °C and 5 °C/min to 280 °C, 10 min isothermal. Quantification was carried out using a low resolution (LRMS) Finnigan MD800 quadrupole as detector in selected ion monitoring mode (SIM). Electron impact (EI) was used as ionisation method for the determination of PCBs and DDTs with metabolites. Negative ionisation mode (NCI) was used to determine the toxaphenes, other chlorinated pesticides and the brominated flame retardants. Methane (5.0 quality) was used as reactant gas. The limit of detection (three times signal/noise) for PCB was between 0.1 and 10 ng/g ww, for the DDT-group between 1 and 7 ng/g ww, for the PBBs/PBDEs between 0.1 and 0.4 ng/g ww, for the toxaphenes between 0.6 and 80 ng/g ww and for the pesticides between 0.2 and 8 ng/g ww.

For the high resolution measurements (HRMS), a VG Autospec was used at a resolution of  $M/\Delta M$  10,000 and 8000 V acceleration voltage using EI and SIM mode. The electron energy was 30 eV and the ion source temperature 240 °C. The two most intensive isotope masses of the molecular mass were monitored for each isomer group.

## 2.3. Quality control

The quality of the methods used is verified regularly in international inter-calibrations between participating institutions (Quasimeme, Toxaphene Round Robin Study II). The use of isotopically labelled internal standards for quantification and the frequent control of complete method blank values insured a high quality of the analytical results. Blank values were not subtracted.

## 3. Results

The samples collected from glaucous gull were from 13 males and nine females. However, sex determination was uncertain for one male and one female (Table 1), since the morphological measurements separating males and females overlapped for these individuals. Selected data for the gulls representing the sample pool are presented in Table 1. The body mass of the gulls from the two sampling areas and sampling periods (1995 and 1999) were comparable when sexes were treated separately,

even though sampling was carried out before and after egg-laying. The average body mass of male and female birds was 1860 g ( $\pm 94$  g) and 1500 g ( $\pm 126$  g), respectively. The average lipid concentration in liver samples was 6.7% ( $\pm 1.5\%$ ) for male and 6.0% ( $\pm 2.3\%$ ) for female birds. The lipid concentration in the intestinal contents was 6.0%.

Spider crab, *Hyas araneus*, dominated the stomach contents of the 15 glaucous gulls sampled on Bjørnøya in 1999. All stomachs contained whole crabs or pieces of crabs. Remains of unidentifiable fish and a fulmar chick (10 cm in length) were found in the stomachs of two gulls. In 60% of the investigated stomachs, remains of feathers and down feathers were also found.

### 3.1. Toxaphene

The livers and the intestinal contents from the glaucous gulls sampled on Bjørnøya in 1999 were analysed for 10 different toxaphene congeners. However, only four toxaphene congeners could be detected in the samples. Toxaphene B9-1679 (Parlar 50), with a median concentration of 15 ng/g ww (2.2–54 ng/g ww, respectively), and B8-1413 (Parlar 26), with a median concentration of 8 ng/g ww (1.2–26 ng/g ww) dominated in all liver samples (Table 2). Two samples from male glaucous gulls had noticeably higher contaminations of B9-1679 and B8-1413, than the other birds (43 and 19 ng/g ww). In the intestinal content sample, the concentrations of B9-1679, B8-1414 and B8-1413 were 50, 12 and 23 ng/g ww respectively. These concentrations are twice as high as the median liver concentrations (Table 2). In contrast to liver samples, the concentration of B7-515 in the intestine sample was below the detection limit.

The liver samples collected in 1995 were only analysed for B7-515, B8-1413, B9-1025 and B9-1679, due to the lack of suitable reference standards at the time when the analyses were performed. The median concentrations of B8-1413 and B9-1679 were almost four times higher in the liver samples from birds collected on Bjørnøya in 1995 (39.4 and 65.0 ng/g ww, respectively) than in the samples collected in 1999. In liver samples, collected in

gulls from Longyearbyen in 1995, the concentrations of B8-1413 and B9-1679 were comparable to levels found on Bjørnøya in 1999 (16.3 and 21.6 ng/g ww, respectively).

### 3.2. Brominated flame retardants

Of the 10 brominated flame retardants measured using LRMS, only PBDE 47 and 99 were detected in the 15 liver samples collected in 1999 (PBDE 47: median of 2.3 with a range of 0.5–22 and PBDE 99 media of 0.9 ng/g ww with a range of <LOQ–7.9). In the two male glaucous gulls with elevated toxaphene levels, higher levels of PBDE 47 (15 and 22 ng/g ww, respectively) than in the other individuals were found. As with toxaphene contamination, the intestinal contents was more contaminated with PBDE 47 and 99 than the liver samples (58 ng/g ww for PBDE 47 and 12 ng/g ww for PBDE 99).

Semiquantitative HRMS analysis of the two liver samples containing the highest levels of toxaphene and PBDEs and the intestinal contents sample revealed the presence of PBDE 100, 153 and 190, as well as several non-identified congeners. Interestingly, the concentrations of PBDE 100 and 153 were in the same order of magnitude as PBDE 47 and 99. Additionally, the HRMS measurements in these three samples revealed the presence of several non-identified PBBs.

### 3.3. Pesticides

Only the liver samples collected in July 1999 were analysed for pesticide contamination. Within the group of analysed pesticides, *p,p'*-DDE was the most abundant pesticide metabolite (median concentration of 890 ng/g ww in liver from males, 286 ng/g ww in liver from females and 780 ng/g ww in intestinal contents). Almost no *p,p'*- or *o,p'*-DDT could be detected in any of the samples (Table 3).

The hepatic and intestinal concentration levels of *cis*- and *trans*- chlordane as well as *cis*- and *trans*- nonachlor were comparable to the toxaphene levels. Mirex, heptachlorepoxyde and oxychlordane were detected in high concentrations in all samples (Table 3). Heptachlor, dieldrin or  $\alpha$ -,  $\beta$ - and  $\gamma$ - HCH were not detected.

Table 2  
Toxaphene concentrations (ng/g ww) in glaucous gull liver samples

| Sampling area |          | <i>n</i> | B8-1413 (Parlar 26) | B7-515 (Parlar 32) | B8-141 (Parlar 40) | B9-1679 (Parlar 50) |
|---------------|----------|----------|---------------------|--------------------|--------------------|---------------------|
| BØ 95         | <i>m</i> | 3        | 39.4                | <LOD               | na                 | 65.0                |
|               | <i>r</i> |          | 24–70               |                    |                    | 41–116              |
| BØ 99         | <i>m</i> | 15       | 8.0                 | 4.6                | 5.7                | 14.9                |
|               | <i>r</i> |          | 1.2–26              | <LOD-7             | 1.3–21             | 2.2–54              |
| LB 95         | <i>m</i> | 4        | 16.3                | <LOD               | na                 | 21.6                |
|               | <i>r</i> |          | 13–25               |                    |                    | 21–40               |

BØ: Bjørnøya; LB: Longyearbyen; na: not analysed; <LOD: less than limit of detection ( $3 \times S/N$ ); *m*: median concentration; *r*: range. The intestinal concentrations are given in the text.

Table 3

Median concentrations of pesticides and PBDEs in liver and intestinal contents of glaucous gulls (ng/g ww) sampled at Bjørnøya 1999; the compounds with levels below LOD in all samples are not presented in the table

| Pesticides and PBDEs    | Liver Median (n = 15) | Range (liver) | Intestinal contents (n = 1) |
|-------------------------|-----------------------|---------------|-----------------------------|
| <i>cis</i> -Chlordane   | 7.3                   | <LOQ – 18.2   | 0.2                         |
| <i>trans</i> -Chlordane | 3.2                   | <LOQ – 3.9    | 0.2                         |
| Heptachlorepoxyde       | 54.9                  | 10.8 – 128.1  | 25.0                        |
| Mirex                   | 54.5                  | 12.2 – 509.7  | na                          |
| <i>trans</i> -Nonachlor | 11.2                  | <LOD – 11.1   | 2.9                         |
| <i>cis</i> -Nonachlor   | 7.6                   | <LOD – 16.1   | 2.1                         |
| Oxychlordane            | 104.4                 | 18.7 – 327.1  | 153.0                       |
| Hexachlorobenzene       | 25.0                  | 6.3 – 91.6    | 96.4                        |
| <i>p,p'</i>             | 368.0                 | 86.2 – 1416.4 | 764.0                       |
| PBDE 47                 | 2.3                   | 0.5 – 22.0    | 58.0                        |
| PBDE 99                 | 0.9                   | <LOD – 7.9    | 12.0                        |

na: not analysed; <LOD: less than limit of detection ( $3 \times S/N$ ); <LOQ: less than limit of quantification ( $10 \times S/N$ )

### 3.4. PCB

There were no differences in PCB concentrations between liver and intestine samples (Fig. 1). PCB 153, 138 and 118 dominated the PCB pattern in both liver and intestinal contents samples (Table 4). The sum of the 35 measured PCBs constituted more than 72% of all analysed halogenated organics in the liver samples (Fig. 2). The two male gulls that showed elevated levels of toxaphene, PBDEs and pesticides had 5-fold higher PCB concentrations as compared to the other liver samples collected in 1999. Liver samples from male

birds, with median sum PCB of 2753 ng/g ww, were more contaminated than samples from female birds (median sum PCB of 1122 ng/g ww). When excluding the two higher contaminated samples from males, the median sum PCB concentration decreases to 2309 ng/g ww in male birds. No difference in the PCB pattern was observed between the two sexes, with and without the higher contaminated samples.

### 4. Discussion

To our knowledge, the present study is the first investigation of toxaphene- and PBDE levels in glaucous gulls.

In the birds sampled in 1999 the levels of toxaphene and PBDEs were low (less than 2% of the overall contamination load) compared to the concentration of other analysed organohalogen compounds (Fig. 2). There is sparse information in the literature about toxaphene contamination in Arctic seabird species. In a study from Greenland, Johansen et al. (2000) found concentrations of total toxaphene between 12 and 53 ng/g ww in liver samples from thick billed murre (*Uria lomvia*), king eider (*Somateria spectralis*) and common eider (*Somateria mollissima*).

Only three samples of male birds with unknown age could be collected in May 1995 on Bjørnøya. The high levels of toxaphene found in these samples are comparable with the levels found in the two samples from Bjørnøya, 1999, which were characterised by elevated levels for almost all analysed components. The wide range of concentrations detected for liver tissue may be due to several factors, like varying migration patterns, feeding behaviour, temporal trends or age differences

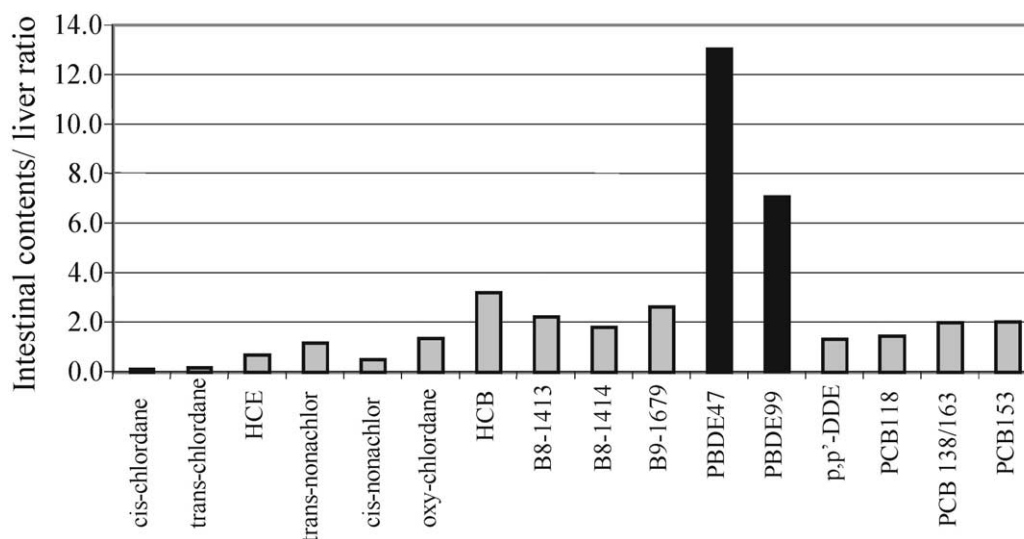


Fig. 1. Intestinal contents/average liver concentration ratios of selected POPs in samples from glaucous gulls (*Larus hyperboreus*) from Bjørnøya, 1999 (HCE: heptachlorepoxyde; HCB: hexachlorobenzene).

Table 4

Median PCB concentrations in liver and intestinal contents of glaucous gulls sampled at Bjørnøya 1999 (ng/g ww); PCB congeners 18, 26, 95, 149, 169 and 174 had levels below LOD in all samples

| PCB          | Liver female  | Range         | Liver male    | Range         | Intestinal contents |
|--------------|---------------|---------------|---------------|---------------|---------------------|
| PCB 28/31    | 1.5 (<LOD)    | < LOD – 6.9   | 4.2 (4.2)     | < LOD – 21.6  | 9                   |
| PCB33        | < LOD         | –             | < LOD         | < LOD – 15.1  | < LOD               |
| PCB33        | < LOD         | < LOD – 112.6 | < LOD         | –             | 12                  |
| PCB 52/49/47 | < LOD         | < LOD – 9.9   | 3.0 (3.5)     | < LOD – 19.7  | 1                   |
| PCB70/74     | 16.6 (12.2)   | < LOD – 54.8  | 78.5 (67.7)   | 25.7– 169.6   | 24                  |
| PCB 76       | 0.9 (0.8)     | < LOD – 3.2   | 4.8 (4.6)     | 1.6– 11.1     | na                  |
| PCB99        | 18.6 (17.3)   | < LOD – 92.2  | 96.7 (139.7)  | 3.68– 308.9   | 238                 |
| PCB101       | < LOD         | –             | < LOD         | < LOD –       | 1                   |
| PCB105       | 29.2 (15.1)   | < LOD – 71.3  | 54.9 (53.9)   | 24.9– 136.8   | 90                  |
| PCB110       | < LOD         | < LOD – 19.8  | 18.1 (20.1)   | < LOD –       | na                  |
| PCB 114      | < LOD         | < LOD – 157.0 | 8.4 (7.1)     | < LOD –       | 14                  |
| PCB118       | 104.0 (58.9)  | 34.9–291.4    | 299.5 (308.4) | 129.6– 965.6  | 370                 |
| PCB126       | < LOD         | < LOD – 13.8  | < LOD         | < LOD –       | na                  |
| PCB128       | 15.9 (6.5)    | < LOD – 31.0  | 25.9 (19.5)   | 8.1– 73.7     | 92                  |
| PCB 138/163  | 217.3 (108.1) | 67.2 – 607.9  | 459.5 (462.8) | 166.9– 2090.6 | 882                 |
| PCB141       | < LOD         | < LOD – 69.9  | 31.0 (31.4)   | < LOD –       | na                  |
| PCB 146      | 61.3 (31.0)   | < LOD – 196.3 | 129.7 (131.3) | 57.8– 655.8   | na                  |
| PCB153       | 324.3 (212.5) | 97.4 – 1004.4 | 832.6 (833.0) | 269.9– 3643.7 | 1482                |
| PCB156/ 157  | 10.8 (8.3)    | 7.1 – 51.3    | 45.4 (46.2)   | 16.5– 167.0   | 130                 |
| PCB167       | 23.3 (<LOD)   | < LOD – 82.5  | 78.0 (67.0)   | 22.1– 190.8   | 53                  |
| PCB170       | 62.6 (16.1)   | < LOD – 130.9 | 106.3 (145.9) | 47.2– 935.7   | 200                 |
| PCB180       | 147.1 (113.9) | 24.1 – 362.7  | 367.2 (443.1) | 119.0– 2705.5 | 627                 |
| PCB183       | 31.4 (23.0)   | 23.0 – 69.6   | 63.4 (85.4)   | 21.0– 461.1   | 121                 |
| PCB187       | 33.5 (10.5)   | < LOD – 55.6  | 54.6 (93.1)   | 25.5– 234.7   | 91                  |
| PCB194       | < LOD         | –             | < LOD         | –             | 58                  |
| Σ PCB        | 1122 (716)    |               | 2753 (3873)   |               | 4503                |

na: not analysed; <LOD: less than limit of detection ( $3 \times S/N$ ); <LOQ: less than limit of quantification ( $10 \times S/N$ ); (n) median value without sample with uncertain sex determination.

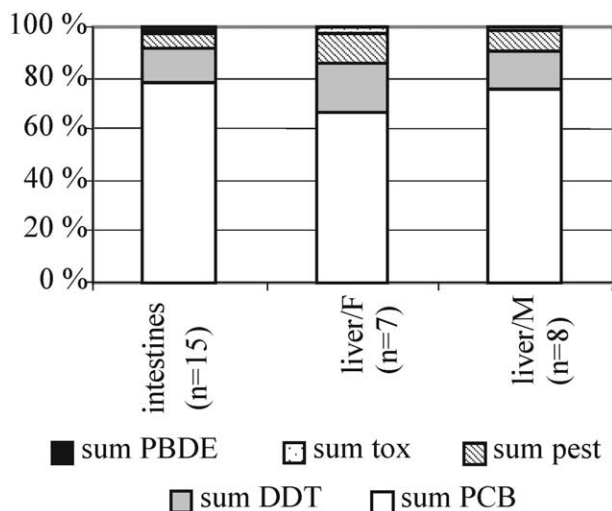


Fig. 2. The relative distribution of analysed POPs in liver and intestinal contents of glaucous gulls (*Larus hyperboreus*) from Bjørnøya, 1999 (F: female; M: male) (tox: toxaphene; pest: pesticides).

between the gulls in the sampling pool (Bustnes et al., 2000; Sagerup et al., 2002).

In contrast to this study are results from studies on harp seal and polar cod from the same region with equal PCB and toxaphene levels (Wolkers et al., 2000).

However, studies which include other Arctic species are needed in order to understand the contribution of toxaphene to the total contaminant burden in the Svalbard area. It is still unclear if the low levels found in glaucous gull are due to elimination processes (metabolism and excretion), migration patterns or simply choice of food items.

When compared to chlorinated pollutants, BFRs were not abundant in glaucous gulls from Bjørnøya. The concentrations of PBDE 47 and 99 were more than 100 times lower than levels of PCB 153 in all analysed samples. However, the levels of the analysed PBDEs congeners were similar to the levels of toxaphene congeners. In addition to the quantified PBDEs, the HRMS analysis indicated a range of different PBDE in glaucous gull.

The present finding of elevated levels of PBDE 47 and 99 in the intestinal contents compared to the liver raises some questions which needs further investigation. One explanation may be poor uptake of these compounds through the gastro-intestinal membranes. The size of the brominated molecules as well as shape and polarity may hinder intercellular transport through the membranes and subsequently lead to increased faecal elimination.

The difference in the intestinal/liver ratio (relation between intestine concentration and average liver

concentration of all 15 liver samples) of PBDE 47 compared to the abundant PCB 153 (13.0 and 2.0, respectively) indicates a less effective uptake of PBDE 47. This is in contrast to findings in pike (*Esox lucius*) where the average uptake efficiency of PBDE 47 and PCB 153 have been estimated to 90 and 75%, respectively (Burreau, 1997).

These findings could also be explained by different transport mechanisms for these two compound groups leading to a different concentration gradient at the time of the sacrifice of the gulls. Finally, the ability of glaucous gulls to efficiently metabolise PBDEs may also be an explanation. However, this is contradicted by the stability of the molecules against biodegradation (Örn and Klasson-Wehler, 1998). The limited number of samples makes it difficult to make final conclusions.

The pesticide metabolites heptachlorepoxide and oxy-chlordane represented 85% of the sum concentration of all measured chlordanes. Oxychlordane alone accounted for 57% of the total chlordanes. One possible explanation for these findings could be a high metabolic capacity for chlordanes compounds in glaucous gull. However, recent results from glaucous gulls show that this species has a low metabolic capacity for PCBs (Henriksen et al., 1998, 2000). Another possible explanation to the high concentrations of metabolic products both in liver and intestines may be that the birds had been feeding on dead marine mammals (Fisk et al., 1999). For the analysed pesticides, no significant concentration differences were found between liver and intestines (Table 3).

The pesticide levels are comparable to levels found in glaucous gulls sampled on Svalbard in 1991 and in Greenland in 1994 (liver samples). Glaucous gulls collected on Bjørnøya in 1995 and 1996 (Savinova et al., 1995; Cleemann et al., 2000; Henriksen et al., 2000) had higher liver-concentrations of some pesticides than the birds analysed in the present study.

PCBs were the dominating POPs in the Bjørnøya samples from 1999 (66% for female and 77% for male glaucous gulls). The PCB group was the only analysed compound group where sex-related differences in accumulation were found. One of the birds for which sex-determination was uncertain (most likely a female) had higher levels (twice as high) of PCB 138, 153, 170 and 180 than the other females. The median values for females with and without this sample (in brackets) are listed in Table 4. The other bird for which with sex-determination was uncertain (most likely a male) showed no irregularities in POP-concentrations when compared to the other males.

In analogy to marine mammals, it seems that female glaucous gulls mobilise and eliminate some of their PCB burden via egg-laying. However, the small number of samples in the present study makes it difficult to draw final conclusions about possible sex differences.

## 5. Conclusions

The load of PCBs and pesticides in glaucous gulls shows no substantial difference compared to earlier sampling campaigns on the Svalbard archipelago (Gabrielsen et al., 1995; Savinova et al., 1995; Borgå et al., 2001; Cleemann et al., 2000; Henriksen et al., 2000; Sagerup et al., 2000; Bustnes et al., 2001). This indicates a stable transport of POPs to remote Arctic areas via air and sea currents during the last 10 years. PBDEs and toxaphenes contributed less than 2% to the analysed contaminant burden. The levels of toxaphene varied considerable between samples both collected in 1995 and 1999. However, it is not possible to draw conclusions about temporal trends based on the very limited material analysed in the present study. The variation in toxaphene levels may be due to differences in age, migration patterns, metabolic processes or choice of food items. Gender related differences in contaminant burden were only seen for PCBs, with higher levels in male gulls. Two male glaucous gulls had two- to 10-fold higher levels of PCB, pesticides (including toxaphenes) and PBDEs than the other samples collected. Differences in migration patterns and feeding habits may be the main reason for these differences between individuals. However, the age of the birds were not determined, so age-related differences cannot be excluded.

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