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Congener-specific accumulation and patterns of chlorinated and brominated contaminants in adult male walruses from Svalbard, Norway: Indications for individual-specific prey selection

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Abstract

Blubber samples from 17 adult, male walruses were sampled in eastern Svalbard and analyzed for chlorinated and brominated contaminants. A wide range of contaminants were detected, including PCBs (mean 2000; 95% range 1165–4005 ng/g lipid), DDE (mean 100: 95% range 50–310) ng/g lipid), chlordanes (mean 2500; 95% range 1347–5009) ng/g lipid, toxaphenes (mean 80; 95% range 51–132 ng/g lipid) and polybrominated diphenyl ethers (PBDEs) (mean15 ng/g; 95% range 9–27 ng/g lipid). PCB and DDE levels were substantially lower than those of animals sampled 10 year earlier in this area, confirming a decreasing trend for these compounds in the Arctic. However, compared to other recently sampled marine mammals from Svalbard, walruses showed relatively high PCB and chlordane levels although they had lower levels of DDE, toxaphenes, and PBDEs, possibly due to species- and location-specific differences in exposure and metabolism.

The range in contaminant levels found within the sample group was vast, despite the fact that the animals investigated were all adult males from the same location. The PCB pattern in highly contaminated animals was different from that in animals with low levels of contamination, with relatively more persistent PCBs in the highly contaminated group. This suggests that the more contaminated animals were feeding at higher trophic levels; possibly targeting seals in addition to mollusks as their prey. This suggestion was reinforced by the fatty acid profiles of the inner blubber layer of walruses with low versus high contaminant levels, which suggested different diets for the two groups.

Keywords: Walrus; Pollution; PCBs; Arctic; Svalbard; Pesticides; PBDEs; Diet

1. Introduction

The walrus (*Odobenus rosmarus*) is an arctic pinniped species easily recognized by the formidable canines protruding from the upper jaw. Walruses live in relatively shallow, coastal areas within the Arctic where they dive to the bottom to forage on their benthic-living food. Adult males can weigh over 1.5 tons while the

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females are smaller and rarely attain body masses above 1 ton (Fay, 1981). Walruses have a circumpolar distribution and are found in the Pacific, Atlantic and Arctic oceans. The Atlantic walrus (*O. r. rosmarus*) ranges from the eastern Canadian Arctic to Nova Zemlya in Russia and consists of several geographically isolated populations; with the animals around Svalbard and Franz Josef Land comprising one such population (Andersen et al., 1998). During the breeding season walruses are often associated with the pack-ice, while at other times of year, especially summer, they haul out in large groups on land. They acquire sexual maturity between 6 and 10 years of age (Fay, 1981). Reproduction is extremely slow with mature females giving birth to a single calf at 3-year intervals. These low reproductive rates, combined with the tendency walruses have to aggregate in huge groups make them particularly vulnerable to over-exploitation and other human-related impacts. Walruses at Svalbard were extensively hunted for several centuries and were at the brink of extinction when they became protected in 1953. Since then the population has gradually increased; the latest survey in 1993 suggested that the Svalbard-Franz Joseph Land population consist of 1450 walruses older than 2 years and an unknown number of calves (Gjertz and Wiig, 1994, 1995). Walruses are adapted to benthic feeding with various mollusks comprising their most important prey (Fay, 1982; Gjertz and Wiig, 1992). However, some individual walrus are known to prey on other pinnipeds, mainly ringed seals (*Phoca hispida*) as well (Fay, 1960; Lowry and Fay, 1984).

It has been well documented that the arctic environment is exposed to a variety of pollutants (AMAP, 1998, 2004). Due to bioaccumulation through the food chain predatory animals are exposed to the highest degree. In mammals exposure to contaminants occurs mainly through their food and ingested compounds are either metabolized or accumulated in lipid-rich tissues, such as the blubber. Being predators, walruses are exposed to relatively high contaminant concentrations (Muir et al., 1992, 1995), particularly those individuals that prey on seals (Muir et al., 1995). Since walruses are long-lived marine predators and, like other pinniped species, go through seasonal lipid cycles, they might be particularly sensitive to contaminants. During molting and breeding walruses mobilize some of their lipid reserves to meet their energy demands, although their lipid cycles are not as dramatic as in some other seal species (Fay, 1982). Consequently, accumulated contaminants are released from these fat depots, enter circulation, and suddenly become bio-available. This may impose brief periods of acute exposure to these animals. Because more than 98% of accumulated contaminants reside in blubber in seals (Stromberg et al., 1990), contaminant concentrations in this tissue may give a record of total accumulation during an animal's lifespan as well as the potential exposure during lipid breakdown.

The arctic archipelago of Svalbard is known to be home to some of the most contaminated arctic animals, with levels in various species exceeding those found in the same species in other arctic areas (Muir et al., 1992; AMAP, 1998, 2004; Wolkers et al., 1998, 1999, 2000). Indications for contaminant-induced biological effects have been found for a variety of arctic species (AMAP, 1998, 2004), including seals (Wolkers et al., 1998, 2000). Therefore, knowledge on contaminant accumulation in different species is essential to assess the risk for contaminant-induced biological effects. However, very few studies exist on contaminant exposure and accumulation in walrus, and data on this species from the Svalbard area are particularly scarce. The few studies that do exist involve a relatively limited set of contaminants, often not presented as individual congeners but as the sum of PCB, chlordanes, DDTs and toaxaphenes (Wiig et al., 2000), making spatial and temporal comparisons difficult. Therefore, the current study was carried out to assess the congener-specific accumulation of a wide range of pollutants, including PCBs, chlorinated pesticides and polybrominated diphenyl ethers (PBDEs), in adult male walruses from Svalbard. In addition, differences in contaminant accumulation pattern and levels were related to possible differences in diet based on fatty acid profiles of the inner blubber layer of these individuals (Skoglund, 2006).

2. Methods

2.1. Sample collection

Blubber biopsies were collected from 17 adult male walruses from the eastern parts of the Svalbard Archipelago during August 2002–04. The walruses were immobilized with an intramuscular injection of ethorphine hydrochloride which was reversed with diprenorphine hydrochloride as described in Griffiths et al. (1993). Standard length (±5 cm) was measured in a straight line from the tip of the snout to the end of the tail. Then the length, and diameter at the base of the tusks, was measured (±1 cm). Walrus tusks grow in length and girth throughout most the animal's life, reaching an asymptotic value when the animals are 20–30 years of age (Fay, 1982). Tusk volume can therefore be used as a crude indicator of age; volume was calculated assuming that the tusks were cone-shaped, and thus the formula

$V = 1/3\pi r^2 * h$ (where r is tusk radius at the base and h is the length of the tusk) was used.

Blubber biopsies were collected using a custom-made hollow stainless steel tube (diameter: 6 mm, length: 150 mm) that was sharpened at one end and attached via the other end to an electrical drill that enabled a rapid, clean cut through the complete blubber layer. The biopsies were taken vertically at a mid dorsal point, approximately 60% of the way down the body from the cranial end; they consisted of the skin and the entire blubber layer down to the muscle (length 7–8 cm). Each biopsy was wrapped separately in aluminum foil and kept frozen (ca. −20 °C) until analysis.

2.2. Chemicals

All chemicals used during the analyses were of pesticide grade and commercially available from Sigma (St. Louis, MO, USA) and Merck (Darmstad, Germany).

2.3. Chemical analyses

Walrus blubber was analyzed for PCBs (IUPAC numbers 19, 18, 16/32, 25/26, 28, 33, 22, 52, 49, 47/48, 44, 64/71/72, 74, 70, 66, 55, 81, 77, 88/95, 91, 92/89/84, 101, 99/113, 97, 85, 110, 118, 114/122, 105, 151, 135/144, 149, 146, 153, 141, 138/164, 162, 128/167, 156, 157, 179, 176, 178, 182/187, 183, 174, 177, 171, 172/192, 180/193, 170/190, 189, 202, 201/204, 197, 199, 196/203, 195, 194, 207, 208, 206, 209), toxaphenes (Parlar 2, 26, 38, 40/41, 44, 50, 62), DDE, HxCBz, chlordanes (*cis*-heptachlorepoxide, *cis*-chlordane, *trans*-chlordane, oxychlordane, MC6, *trans*-nonachlordane, *cis*-nonachlordane), and PBDEs (28, 47, 66, 85, 99, 100, 138, 153, 154, and 183). About 1 g of tissue from each blubber sample was homogenized in a mortar with sodium sulphate (1:5). About 5 g of the homogenate was packed into a Suprex standard extraction vessel (10 ml). An internal standard, consisting of a mixture of ^{13}C-labeled PCBs and PBDEs, was added before the SFE extraction. On the top of the sample approximately 4.5 g of basic aluminum oxide (AlOx) was added as a fat retainer. The extractions were carried out on a Suprex Autoprep/Accutrap SFE using CO_2 as the supercritical fluid. The chamber temperature was 40 °C and the pressure was 280 bar during extraction which took place at a flow rate of 2 ml/min for 25 min. All the analytes were trapped on a C18 solid sorbent (ODS, Octadecylsilica). The restrictor and trap temperatures were kept at 45 °C and 40 °C respectively. After completion of the extraction the trap was rinsed with 3.5 ml hexane and 3.5 ml methylene chloride at a rate of 2 ml/min. The recovery standard, containing ^{13}C-labeled PCB 128 and 178, was then added and the sample volume was reduced to 30 μl tetradecane, producing an extract ready for GC/MS analysis. Separate lipid determinations were performed by putting some (~1 g) of the homogenate in a small column and quantitatively extracting the lipid with methylene chloride and hexane (1:1). The weight of the extracted lipids was determined gravimetrically.

Selected ion SIR HRGC/LRMS spectra were recorded using an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer (HRGC/LRMS) used in the selected ion recording mode (SIR). Chromatographic separation was achieved by split-less injection of 2 μl on a non-polar DB-5 column using helium as the carrier gas. The GC oven was programmed as follows: 180 °C initial hold for 2 min increase at a rate of 15 °C/min to 205 °C; followed by an increase of 3.7 °C/min to 300 °C; and final hold at 300 °C for 15 min. For PCB and pesticide analysis the two most abundant ions of the molecular ion cluster were monitored, in addition to masses for the ^{13}C-labeled internal standards using EI ionization. Quantification was done using a standard containing the internal standard, the recovery standard and a mixture containing the different chlorinated pesticides and at least one PCB at each chlorination level. PBDE and toxaphene analyses were done using NCI ionization monitoring *m*/*z* 79/81 for the PBDEs and the most abundant masses of the most abundant fragment for the toxaphenes.

The detection limit (DL) was set at a signal to noise ration of 3 (S/N > 3) and depended on the amount of lipids extracted. A blank sample was run with each set of samples, no blank levels > 10% of the levels measured in the samples were observed. A QA/QC sample (human adipose tissue) was analyzed with each set of 10 samples and was within the QA/QC criteria of 20% RSD. The SFE-LC method has been tested thoroughly on different certified reference material for both the target compounds of this study and dioxins (van Bavel et al., 1995, 1996). The laboratory participates regularly in international QA/QC studies for the target compounds (AMAP, BSEF) which showed acceptable *z*-scores <2 for all compounds (PCBs, Pesticides and BDEs).

2.4. Fatty acid analyses

Subsamples of approximately 30 mg were cut from the innermost blubber of each biopsy. Fatty acid analyses were carried out as described by Grahl-Nielsen et al. (2003). Briefly, samples were placed in 15-ml glass tubes and 500 μl HCl/MeOH (hydrochloric acid/

methanol) was added. Blanks were prepared using similar procedures. All tubes where securely closed with Teflon®-lined plastic screw caps and left in an oven, at 90 °C for 2 h, for methanolysis. After cooling, approximately half of the remaining liquid in the tubes was evaporated using N_2 gas. Extraction of the sample was performed by adding 1 ml distilled water and 1 ml hexane. After mixing, the sample was centrifuged at 3000 rpm for 3 min and the hexane removed for analyses. A second extraction was performed using hexane only. The extracts were analyzed by GC (Hewlett Packard HP 5890 II with Hewlett Packard 7673A auto sampler), with a silicon-lined CP-WAX 52 CB (polyethylene glycol) column of 25 m × 0.25 mm, and a 0.2-μm-thick stationary phase. The carrying gas was helium which was run at 1.7 ml/min, at 40 °C. Pure hexane and a standard solution, consisting of 20 known fatty acid methyl esters (Nu-Chek-Prep, Elysian, Minn., USA), were as standards. Data from the GC were recorded in the software Atlas 2000 (Thermo Labsystems). Fatty acids were named according to the nomenclature guide lines of IUPAC (International Union of Pure and Applied Chemistry).

2.5. Data management

Based on the chlorine substitution pattern on the *ortho* (*o*), *meta*(*m*), and *para* (*p*) positions four groups of PCB congeners, with a different resistance towards metabolic breakdown (metabolic groups), were assigned (Boon et al., 1992; Bruhn et al., 1995). Group I: congeners with no vicinal H-atoms in *o,m* or *m,p* positions, are considered persistent (PCBs 146, 153, 167, 178, 180, 183, 189). Group II: congeners with vicinal *m,p* H-atoms and 0-3 *o*-Cls, which are thought to be metabolized by CYP 2B/3A and to a lesser extent CYP1A enzymes (PCBs 52, 66, 101, 110, 149, 174). Group IIIa: congeners with no vicinal H-atoms at *m,p* positions, and a maximum of 1 *o*-Cl, which are thought to be metabolized by CYP1A (PCBs 28, 74, 105, 114, 118, 156, 157). Group IIIb: congeners with no vicinal H-atoms at *m,p* positions, and 2 or more *o*-Cls, are considered persistent (PCBs 99, 128, 138, 170, 171, 177).

Geometric means and 95% confidence intervals were calculated for concentrations of individual contaminants. The relative presence of the various contaminants groups, i.e. PCBs, DDE, chlordanes, toxaphenes, and PBDEs, was expressed as percent of total contaminants measured.

Based on the levels found, 2 groups of walruses were distinguished: a 'low' group with total levels of PCB 153 below 1500 ng/g lipid and a 'high' group with levels exceeding 1500 ng/g lipid. Differences in contaminant patterns between the groups were assessed using Student's *t*-test.

The fatty acid profiles were calculated for all individuals in the low and high groups, however, due to analytical problems, two samples were lost in the laboratory. Calculations and statistical analyses were based on the 22 fatty acids that were the most important components of the blubber. The integrated chromatogram values were normalized to express the value of each fatty acid as a percentage of the total amount of fatty acids. For details on the fatty acid profiles, see Skoglund, 2006. These relative values were transformed logarithmically prior to further statistical analyses. All data were subjected to Principal Component Analysis (PCA) (Wold et al., 1987) using the software SIRIUS 7.0 (Kvalheim and Karstang, 1987) from Pattern Recognition Systems.

3. Results

PCBs and chlordanes were the dominant contaminant groups found in the walrus samples, with average levels of about 2500 ng/g. But the range was large, extending between 264 and 12,702 ng/g lipid for PCBs and from 265 to over 35,000 ng/g lipid for chlordanes (Table 1). PCB153, 138, and 180 accounted for more than two thirds of total PCBs, while the metabolite oxychlordane was by far the most dominant chlordane compounds, accounting for about 80% of total chlordanes. DDE levels were on average much lower than PCBs and chlordanes, but the range was even larger, roughly between 5 and 5000 ng/g lipid (Table 2). Total toxaphenes measured were below 100 ng/g lipid (Table 2), with the range between 27 and 671 ng/g lipid. Toxaphene congeners 2, 38, and 62 were below detection in all samples. Tox 26 was quantitatively the most important toxaphene, contributing over 60% to total toxaphenes measured. PBDE levels were also low with average levels about 15 ng/g lipid, but again a large range, from 2 to 75 ng/g lipid was seen.

The contaminant pattern, i.e. the presence of main contaminant groups expressed as a % of total contaminants measured, showed a relatively high proportion of both PCBs (43%) and chlordanes (49%), while percentages of toxaphenes, DDE, and PBDEs were surprisingly low, i.e., 2.0, 3.7, and 0.3% respectively (Fig. 1).

There was no difference in body length between the low and high contaminated groups, nor was there any difference in tusk volume. However, there were substantial differences in both contaminant concentrations as well as contaminant patterns (Fig. 2) between

Table 1
Geometric mean PCB concentrations (ng/g lipid), 95% confidence limits, and the range in blubber of adult male walruses from Svalbard, Norway

PCB congener	28	52	66	74	99	101	105	110	114	118	128	138	146	149	153	156	157	167	170	171	174	177	178	180	183	189	∑PCB
Group	IIIa	II	II	IIIa	IIIb	II	IIIa	II	IIIa	IIIa	IIIb	IIIb	I	II	I	IIIa	IIIa	I	IIIb	IIIb	II	IIIb	I	I	I	I	
Mean	1.2	0.3	1.0	6.4	62.5	2.1	29.5	0.2	0.4	80.3	15.1	292.8	31.2	0.5	1126	2.9	2.9	0.2	54.7	4.6	0.0	0.7	32.6	229.2	23.5	0.0	2160
95% low	0.8	0.1	0.5	3.7	24.0	0.9	13.4	0.1	0.2	40.1	5.2	127.9	13.1	0.2	663.3	1.4	1.4	0.1	24.2	1.9	0.0	0.3	19.3	114.9	9.4	0.0	1165
95% high	1.8	0.6	2.0	11.1	162.5	4.8	65.0	0.5	0.9	161.1	44.1	670.2	74.7	1.3	1912	6.0	6.0	0.7	123.3	11.3	0.1	1.7	55.0	457.3	58.6	0.1	4005
Range	0.4–8.3	0.04–6.1	0.2–14.9	0.8–39.7	4.5–670.4	0.13–42.6	1.6–239.6	0.0–4.2	0.0–5.5	5.4–494.8	0.6–314.9	18.3–2751	1.4–439.5	0.1–10.6	144.3–6380	0.3–29.8	0.4–18.6	0.0–15.5	4.3–515.0	0.2–65.4	0.0–0.72	0.1–11.0	5.6–204.9	27.8–1736.6	1.3–344.3	0.0–0.3	264.1–12702

The groups are based on the chlorine substitution pattern of the PCB congener. Group I: no vicinal H-atoms in *o,m* or *m,p* positions. Group II: congeners with vicinal *m,p* H-atoms. Group IIIA congeners with no vicinal H-atoms at *m,p* positions, and a maximum of 1 *o*-Cl. Group IIIB: congeners with no vicinal H-atoms at *m,p* positions, and 2 or more *o*-Cls.

Table 2
Geometric mean pesticide and polybrominated diphenyl ether (PBDE) concentrations (ng/g lipid), 95% confidence limits, and range in blubber of adult male walrus from Svalbard, Norway

	Tox 26	Tox 40/41	Tox 44	Tox 50	∑Tox	p,p DDE	c-chl	t-chl	c-nona	t-nona	Oxy	Hept	MC 6	∑chl	HCB	∑Pest.	BDE 28	BDE 47	BDE 99	BDE 100	BDE 138	BDE 153	BDE 154	∑BDE
Mean	51.4	1.7	10.8	14.9	82.0	123.8	8.6	2.8	0.8	35.7	2047	58.0	276.5	2598	0.3	2991	0.1	7.2	1.5	0.3	0.5	0.9	2.7	15.6
95% low	31.2	1.2	7.5	8.9	51.0	49.5	4.5	1.4	0.4	15.6	1036	34.4	135.9	1347	0.2	1635	0.0	3.7	0.9	0.2	0.3	0.5	1.7	9.2
95% high	84.8	2.3	15.6	25.1	131.8	309.5	16.6	5.8	1.5	81.8	4045	98.1	562.7	5009	0.6	5469	0.1	13.8	2.7	0.6	0.8	1.7	4.3	26.7
Range	11.4–116.9	0.5–4.7	4.5–31.0	2.5–66.1	27.4–671.5	4.6–5065	0.9–81.5	0.3–38.9	0.1–6.0	2–1192	223–33327	13.1–797	23–3474	265–37699	0.1–3.0	322.5–39471	0.0–0.5	1.0–61.8	0.2–11.2	0.0–2.0	0.1–3.6	0.1–3.8	0.5–14.4	2.1–r75.9

Tox=toxaphene congener (Parlar 26, 32, 40, 44, 50); ∑Tox=total toxaphene levels; DDT=dichlorodiphenyltrichloro ethane; DDE=dichlorodiphenyldichloroethylene; DDD=dichlorodiphenyldichloroethane; ∑DDT=total DDT levels; c=*cis*; t=*trans*; chl=chlordane; nona=nonachlor; oxy=oxychlordane; hepta=heptachlorepoxide; ∑chl=total chlordane levels; HC=hexachlorobenzene; HCH=hexchlorocyclohexane; ∑HCH=total HCH levels; ∑pest=total pesticide levels; BDE=brominated diphenyl ether.

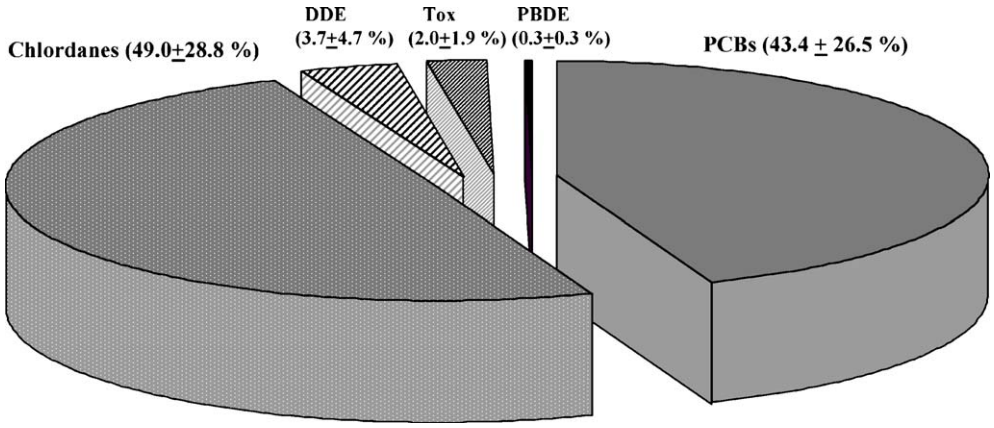

Fig. 1. Overall contaminant pattern in male walrus blubber, expressed as percent of total contaminants measured.

these animals. All contaminant groups, except the chlordanes, showed significantly higher concentrations in the high group (Fig. 2A). A significantly higher relative presence of the more persistent PCBs from groups I and IIIb was found in the high group, while the pattern for less persistent PCBs from groups II and IIIa was largely similar (Fig. 2B). In contrast, only PBDE 99 differed between the low and the high groups, with higher fractions in the lower contaminant group (0.45% versus 0.07% of PCB 153). No differences between high and low contaminated groups could be found for the pesticides (data not shown).

The principal component plot of fatty acids profiles of the inner blubber layer of individual walruses shows, except for one outlier, a clear separation into two different groups for the low and the high contaminated animals (Fig. 3).

4. Discussion

The most recent data on contaminant accumulation in walrus from Svalbard were analyzed in tissues sampled more than a decade ago (Wiig et al., 2000) and in both studies only a limited set of contaminants were analyzed. To our knowledge, the current study is the first to report an extensive range of contaminant levels, including brominated flame retardants, in walruses from Svalbard. The most surprising result was the degree of individual variation in contaminant levels and patterns seen in this very homogenous group which consisted solely of adult males from a restricted geographic area.

Compared to male walruses from Svalbard sampled in the early nineties (Wiig et al., 2000), levels of PCBs in the walruses from the present study were substantially lower: PCB 153, a good reference congener for PCB exposure due to its persistence, was about 1000 ng/g lipid, about 4 times lower, while DDE levels were about 125 ng/g lipid, about 10 times lower. These low levels are in accordance with the general pattern of decreasing exposure to PCBs and DDTs in the arctic environment (AMAP, 2004). In contrast, oxychlordane was over 2000 ng/g lipid in the current study, about 1.5 times higher than in the walruses from the earlier period. However, comparisons like these have to be done with caution, even with animals from similar sex and age, since area- and individual-specific food preferences may have a lot of influence. Walruses feed principally on benthic mollusks which have relatively low contaminant levels (Fay, 1982; Gjertz and Wiig, 1992). However, depending on the area, preying on seals also supplies a varying proportion of the diet (Fay, 1960; Lowry and Fay, 1984), which can have dramatic influence on contaminant exposure and accumulation (Muir et al., 1995).

Also comparing the levels and patterns between species has its limitations due to dietary differences as well as differences in the ability to metabolize contaminants (Wolkers et al., 2004). Compared to other marine mammals from Svalbard, PCB and chlordane levels were generally higher in the walrus, while *p,p*-DDE and PBDEs were generally lower. Male harbor seals (*Phoca vitulina*) and ringed seals, sampled on Svalbard's west coast in the early 2000s (Wolkers et al., 2004) and mid nineties (Wolkers et al., 1998), respectively, showed PCB 153 levels about 500 ng/g lipid, that is half to the value found in the walruses. In contrast, *p,p*-DDE was 10 times higher in the seals: over 1000 ng/g lipid. Similarly, white whales (*Delphinapterus leucas*) sampled from the east coast of Svalbard showed only a third of the level of PCB 153 (about 300 ng/g) as compared to the walruses, while *p,*

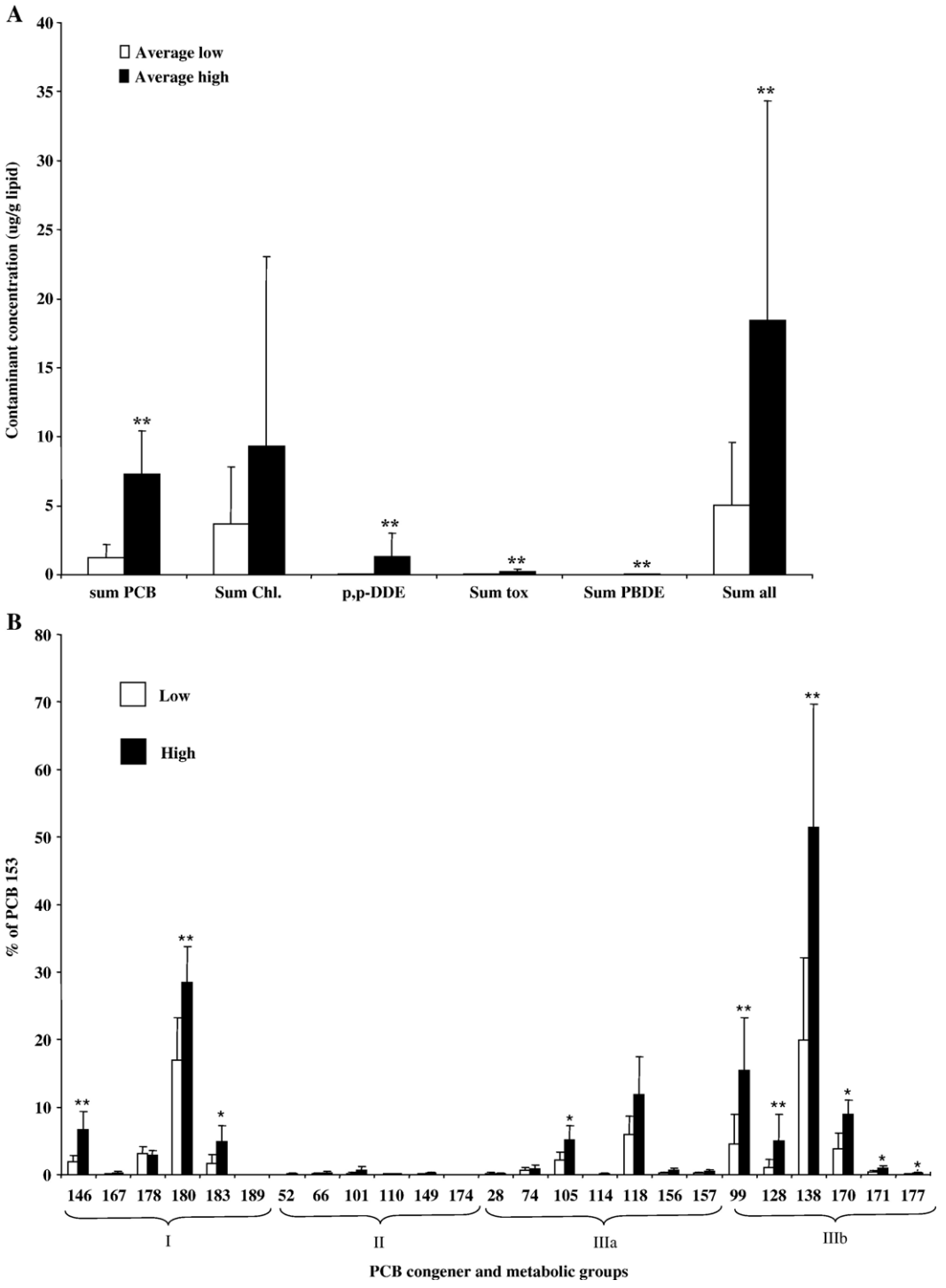

Fig. 2. (A) Concentrations of different contaminant groups in high and low polluted walrus males from Svalbard. PCB = polychlorinated biphenyls; Chl. = chlordanes; DDE = dichlorodiphenyldichloro-ethylene; Tox = toxaphene; PBDE = polybrominated diphenyl ethers. **: Difference significant at $p < 0.001$. (B) PCB congener pattern, expressed as the percent of PCB 153 per metabolic group for high and low contaminated male walrus. Group I: persistent congeners with no vicinal H-atoms in *o,m* or *m,p* positions; group II: congeners with vicinal *m,p* H-atoms and 0-3 *o*-Cls, considered to be metabolized by CYP 2B/3A and to a lesser extent CYP1A enzymes; Group IIIa: congeners with no vicinal H-atoms at *m,p* positions, and a maximum of 1 *o*-Cl, considered to be metabolized by CYP1A; Group IIIb: persistent congeners with no vicinal H-atoms at *m,p* positions, and 2 or more *o*-Cls. *: Difference significant at $p < 0.05$, **: difference significant at $p < 0.001$.

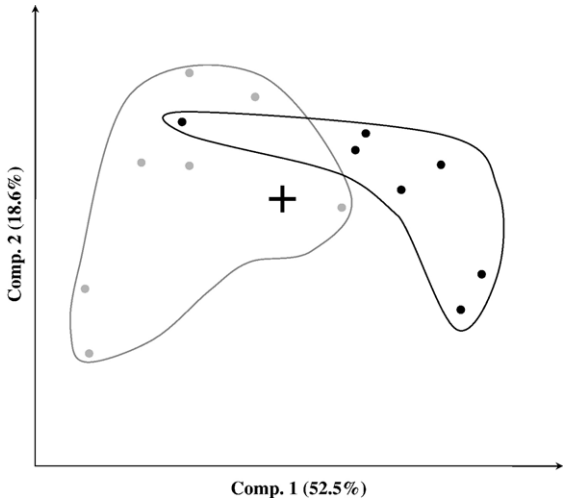

Fig. 3. Principal component analyses plot showing the relation between the fatty acid profile from individual male walruses with high (black dots) and low (grey dots) contaminant levels.

p-DDE was between 1000 and 1500 ng/g lipid in the white whales, that is, about 10–15 times higher (Wolkers et al., 2006). Similar to PCB 153, chlordane levels were also about a third in the white whales as compared to the walruses. In contrast, PBDE 47 was 10 times lower in the walruses (i.e. 7. 2 ng/g lipid) as compared to the whales. These differences between species are most likely caused by a combination of species-specific differences in contaminant metabolism, differences in feeding habits, and perhaps also different spatial use patterns over the annual cycle. It has been well established that metabolic capacity for contaminant breakdown differs between cetaceans and pinnipeds, with a reduced capacity seen in cetaceans (White et al., 1994; Wolkers et al., 2006). In line with these results, the pattern in walrus resembled those in ringed seals with a relatively low presence of PCBs from group II as compared to the white whales, suggesting that cytochrome P450 enzymes from the 2B or 3A family are more active in walrus than in white whales. However, since the diet of the walrus is variable and was not included in this study, the presence and activity of the different CYP enzymes remains largely speculative. Another reason for the differences in contaminant levels between species is due to differences in geography. Contaminant patterns from west and eastern Svalbard differ, possibly due to the differences in water masses reaching the two sides of the archipelago; the influence of Russian industrial and agricultural activities via Russian rivers draining into the Arctic Basin being felt most strongly on the eastern side of Svalbard (Wolkers et al., 1998, 2000).

The walruses from the present study had contaminant concentrations that generally fell within the range of levels found in male walruses from the Canadian Arctic sampled in the late eighties and early nineties (Muir et al., 1995), but similar to the present study Muir et al. (1995) reported large amounts of variation within the group studied as well as between different areas. In spite of decreasing PCB and DDT exposure over time (AMAP, 2004), PCB 153, *p,p*-DDE, and total chlordanes were all about 2 to 20 times higher in the Svalbard walrus compared to walruses from Canada that were sampled 10 years earlier, with the exception of the Inukjuak area where PCB 153, *p,p*-DDE, and chlordane levels exceed those in Svalbard animals (Muir et al., 1995). This is likely because walruses in Inukjuak feed a lot on ringed seals. However, since the proportion of seals in the diet of both the Svalbard and Canadian walruses is not precisely known, these comparisons are rather speculative.

Similar to ringed and harbor seals from Svalbard (Wolkers et al., 1998, 2004) the overall PCB pattern in walruses from the present study was characterized by a relatively low representation of the less persistent PCBs (i.e., groups II and IIIa), while the more persistent PCBs were relatively more prevalent. This might indicate that PCB metabolism is walruses is similar to other pinnipeds (Muir et al., 1995; Wolkers et al., 1998, 2004).

The contaminant patterns of the walruses showed relatively large contribution of PCBs and chlordanes, while toxaphene, DDE and to a lesser extent also the PBDEs, were substantially lower compared to 2 cetacean species from Svalbard, i.e., white whales and narwhal (*Monodon monoceros*) (Wolkers et al., 2006). These differences might reflect differences in diet as well as metabolic capacity. The relatively low contribution of less persistent PCBs from groups II and IIIa, toxaphenes, and DDE relative to cetaceans (Wolkers et al., 2006) might be due to a more efficient metabolism of these compounds in the walrus. However, dietary differences might also contribute to these species-specific patterns.

In spite of the homogenous group sampled in this study – all animals were adult males from the same geographical area – a vast range in contaminant concentrations was found and contaminant patterns differed substantially within the group. Positive relationships between age and contaminant concentrations have been established in several walrus studies (Born et al., 1981; Addison et al., 1986; Muir et al., 1988, 2000). However, no correlations between contaminant levels and age (expressed using both body length and tusk

volume) were found in the present study, indicating that the large variations in contaminant levels are due to other factors, such as variation in feeding habits.

Due to selective metabolism and accumulation, tissues of animals feeding higher in the food chain, such as mammals and birds, generally contain proportionally more persistent contaminants than lower trophic level animals such as fish and mollusks (Muir et al., 1995; AMAP, 2004; Wolkers et al., 2004, 2006). It is therefore conceivable that seal-eating walruses will not only show higher contaminant levels, but also different contaminant patterns as compared to the more walruses that consume mainly mollusks, with a higher representation of the more persistent compounds. In addition, the pattern might become even more distinct by selective contaminant metabolism. Due to the more contaminated diet of the seal-eating walruses, xenobiotic metabolizing enzymes, such as the hepatic cytochrome P450 enzymes, might increase their activity, resulting in the selective metabolism of PCBs from groups II and IIIa, resulting in a higher relative presence of the more persistent PCBs. The PCB patterns of the high level animals from the present study clearly showed most similarities with the seal-eating walruses from Inukjuak (Muir et al., 1995), with similarly low contributions of non-persistent PCB congeners (groups II and IIIa) and similarly high contributions of persistent PCBs (groups I and IIIb). It is therefore plausible, and in agreement with the conclusion of Muir et al. (1995), that the high-contaminated individuals from the present study have a larger proportion of seals in their diet compared to the low-contaminated group. This conjecture was supported by fatty acid profiles for the walruses. Although there is considerable debate as to what degree fatty acid profiling can be used in assessing the diet of marine mammals (e.g., Iverson et al., 2004; Grahl-Nielsen et al., 2004; Thiemann et al., 2004), there is a general consensus that major differences in diet will affect the fatty acid profiles of the inner blubber layer (Iversen et al., 1997; Andersen et al., 2004; Grahl-Nielsen et al., 2003). The clear separation of high and low contaminated walruses into two different clusters in PCA analyses of fatty acids from their blubber, suggests differences in diet between these 2 groups that is likely due to a varying proportion of seals in the diet of individual animals.

5. Conclusion

The current study has revealed a wide range of contaminants in walruses from Svalbard with relatively high levels of PCBs compared to other marine mammals from this area. Compared to walruses sampled a decade ago, levels seem to be declining. Differences in PCB pattern between high and low contaminated walruses as well as differences in fatty acid profiles of their inner blubber layer, suggest that these walruses have variable feeding habits, and that the most contaminated animals likely have a significant contribution of seals in their diet.

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