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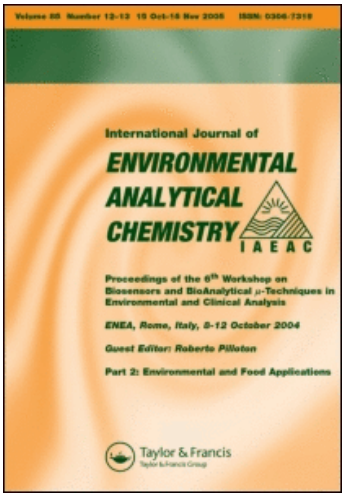

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Levels and Enantiomeric Ratios of Chlorinated Hydrocarbons in Livers of Artic Fox (*Alopex Lagopus*) and Adipose Tissue and Liver of a Polar Bear (*Ursus Maritimus*) Sampled in Iceland

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LEVELS AND ENANTIOMERIC RATIOS OF CHLORINATED HYDROCARBONS IN LIVERS OF ARCTIC FOX (*ALOPEX LAGOPUS*) AND ADIPOSE TISSUE AND LIVER OF A POLAR BEAR (*URSUS MARITIMUS*) SAMPLED IN ICELAND

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Polychlorinated biphenyls (PCBs), oxychlordane, DDT and its metabolites, hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), and compounds of technical toxaphene (CTTs) were quantified by gas chromatography and electron capture detection in livers of ten arctic foxes (*Alopex lagopus*) and in liver and adipose tissue of a polar bear (*Ursus maritimus*) sampled in Iceland. Enantiomeric ratios of oxychlordane and other chiral organochlorines were determined after gas chromatographic enantioseparation on two chiral stationary phases.

The organochlorine pattern of the livers of arctic foxes was dominated by oxychlordane. The enantiomeric ratio of oxychlordane was >1 with the exception of the sample with the highest oxychlordane level. This result was confirmed by gas chromatography-mass spectrometry. PCB congeners and other organochlorines were only lowly abundant. PCB congeners were topped by PCB 180. The samples were from two independent populations, one feeding on the marine and the other feeding on the terrestrial food web. Levels of chlorinated hydrocarbons reflected the different food habits of the arctic foxes from coastal and inland habitats.

Liver and adipose tissue of the polar bear showed deviating levels and ratios of the contaminants. Oxychlordane and p,p'-DDD were the only compounds found in greater abundance in liver than in adipose tissue. All other compounds were more abundant in adipose tissue. Enantiomeric ratios of oxychlordane, α-HCH, B8-1413 (Parlar #26), and

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B9-1679 (Parlar #50) were >1 if the compounds were detected in the polar bear samples.

Keywords: Chlorinated hydrocarbons; gas chromatography; enantiomer separation; Arctic fox (*Alopex lagopus*); polar bear (*Ursus maritimus*)

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INTRODUCTION

Lipophilic and persistent chlorinated pesticides and industrial chemicals are those most likely to bioaccumulate in biota.[1] Atmospheric long range transport led to the fact that these xenobiotics are ubiquitous contaminants in our days.[2] Consequently, the determination of organochlorine residues in biota is a subject of monitoring programmes all over the world. Iceland is a subarctic region located between two major industrial and agricultural zones, North America and Europe. Despite the geographical importance of Iceland, only a few reports on organochlorine levels in Icelandic mammals or birds have been published since 1990.[3-6] Due to the low human population density and the limited expanse of productive land, the use of chlorinated hydrocarbons for industrial and agricultural applications in Iceland is very low although not prohibited. However, an increasing number of toxic persistent organochlorines have been detected in remote areas such as polar regions.[7] The bulk of organochlorine compounds present in Icelandic samples is most probably transported by atmospheric and water long-range transport from Northern America and Europe. This was confirmed by our former studies on two seal species.[3, 5]

In the present study we have focused on analysis of livers of arctic foxes (*Alopex lagopus*). Polychlorinated biphenyls (PCBs), DDT and its metabolites, hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), chlordane-related compounds including oxychlordane, compounds of technical toxaphene (CTTs) were quantified by GC/ECD. Furthermore, we determined the enantiomeric ratios of oxychlordane, α-HCH, B8-1413 (Parlar #26), and B9-1679 (Parlar #50), if those compounds were present in the samples. Data on organochlorine levels in arctic fox are also barely available.[8-9] However, these studies allowed us to evaluate the levels determined in the samples on Iceland. Furthermore, we analyzed adipose tissue and liver of a polar bear (*Ursus maritimus*) killed just off the northwest shores of Iceland. Polar bears and arctic foxes accumulated similar PCB patterns in the respective tissue.[9] Although the number of samples available for this study was comparably small, the results showed significant differences dependent on the habitat of the animals and gives new insights into the pollution of this subarctic region.

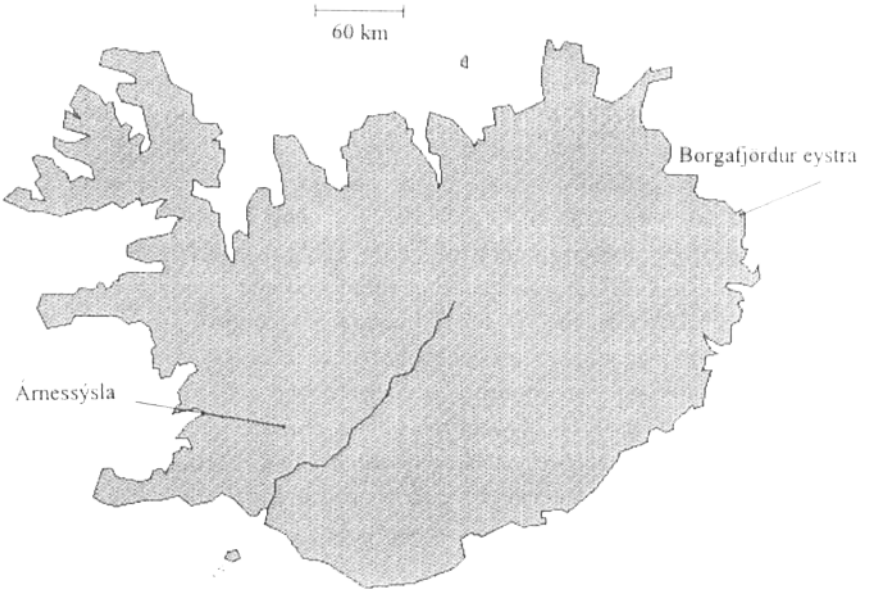

FIGURE 1 Map of the sampling sites in Iceland

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MATERIALS AND METHODS

Samples

Livers were sampled from six female (three subadult, three adult) and four male (one subadult, three adult) arctic foxes (*Alopex lagopus*) which were caught in 1993 and 1994 in two independent populations of Iceland. Six foxes originated from the inland habitat in Árnessýsla, South-Iceland, but the remaining four were sampled in the coastal area of Borgarfjördur eystri, East-Iceland Figure 1). The distance between the two habitats is approx. 300 km and there is no contact between the two populations. Liver and fat samples were collected from a mature, three and half year polar bear (*Ursus maritimus*) accidentally killed on June 24, 1993 close to the pack ice, 64 nautical miles (118.5 km) north of Horn, Northwest-Iceland. Ages of the arctic foxes and the polar bear were determined by counting dental cementum annuli.[10]

Sample Clean-up and Quality Control

The sample clean-up was earlier described in detail.[3, 11] In brief, 2 g of the tissues were digested with perchloric acid/acetic acid (1:1) and extracted twice

with n-hexane. Sample matrix was destroyed with several portions of sulphuric acid. Last remainders of the matrix were separated on silica. For quantitative elution of HCH isomers, 3 g deactivated silica (30% water) were eluted with 60 mL n-hexane.[11] With this method the institute has successfully participated in an intercalibration exercise.[12] The recovery, tested with 60 organochlorine compounds, was generally >75%.[11] We applied perdeuterated α-HCH (α-PDHCH) as recovery standard to monitor presumable loss of high volatile α-HCH during sample concentration steps.[13] Recoveries of α-PDHCH were >80% in all samples. α-PDHCH was recently synthesized and is now commercially available from Promochem (Wesel, Germany). All samples were analyzed in duplicates and the variations were generally below 10%. It was required that the value on one column was confirmed on the second GC column. In case of deviations (coelutions), the lower value was considered. Levels were not extrapolated to 100% recovery but represent the real determined levels. The lowest value that was considered was 1 μg/kg tissue, and levels below this target value were not quantified. All levels are on the basis of wet weight.

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Chemicals

A certified PCB standard solution consisting of PCB 18, PCB 28, PCB 31, PCB 44, PCB 52, PCB 101, PCB 118, PCB 138, PCB 149, PCB 153, PCB 180, and PCB 194) (SIGMA-Aldrich, Deisenhofen, Germany), PCB 170 (Promochem, Wesel, Germany), Pesticide Mix 11 (α-HCH, β-HCH, γ-HCH, δ-HCH, and HCB), ϵ-HCH (internal standard), p,p'-DDD, p,p'-DDE, and p,p'-DDT (Dr. Ehrenstorfer, Augsburg, Germany), each 10 ng/μL, were combined to quantitation standard solutions. A second quantitation standard was composed of 10 ng/μL solutions of oxychlordane, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, and the compounds of technical toxaphene (CTTs), B8-1413 (Parlar #26) and B9-1679 (Parlar #50), all from Dr. Ehrenstorfer. PCB 163 and PCB 99 (Dr. Ehrenstorfer) were used as single standards. Enantioenriched oxychlordane with 75% enantiomer excess of (+)-oxychlordane was from Dr. Ehrenstorfer. Enantioenriched α-HCH was prepared in our lab by enantioseparation on chiral high pressure liquid chromatography as recently described.[14]

Analytical Methods

Analyses were performed on an HP 5890 II gas chromatograph (Hewlett-Packard, Germany) equipped with an inlet splitter which divided the samples on two capillary columns and two ^{63}Ni electron capture detectors (ECDs). Nitrogen was used as carrier (head pressure 0.85 bar) and make-up gas. The samples were

automatically (HP 7673 autosampler) injected in the splitless mode (2 min). The injector and detector temperatures were 220°C and 300°C, respectively. All fused silica capillary columns were from Chrompack (Middelburg, The Netherlands). The standard GC columns combination of this study was CP-Sil 8/C 18 20% together with CP-Sil 19 (both 50 m length × 0.25 mm internal diameter (i. d.) × 0.25 μm film thickness (d_f)). The GC oven program was as follows: 75°C (1.5 min), 25°C/min to 200°C (2 min), 2°C/min to 250°C (1 min), 15°C/min to 280°C (35 min). For determination of PCB 163 we applied a CP-Sil 2 column (63 m × 0.25 μm i. d. × 0.12 μm d_f) with the following temperature program: 60°C (1.5 min), 40°C/min to 200°C (2 min), 2°C/min to 250°C (5 min), 6°C/min to 270°C (50 min).

Enantioseparations were carried out on an HP 5890 II gas chromatograph equipped with a ^{63}Ni ECD detector. Nitrogen was applied as carrier and make-up gas. Enantiomers of α-HCH and oxychlordane were separated on 35% heptakis(6-*O*-*tert*.-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin diluted in OV-1701 (β-TBDM). Unfortunately, we recently described β-TBDM as 6-*O*-t-butyl.-2,3-di-*O*-methyl-β-cyclodextrin[6] instead of the correct name above. The β-TBDM column was a prototype (20 m × 0.25 i. d. × 0.15 μm d_f) obtained from M. D. Müller (Eidgenössische Forschungsanstalt Wädenswil, Switzerland). The GC oven program for β-TBDM was 60°C (2 min), 25°C/min to 160°C (10 min), 1°C/min to 200°C, 10°C/min to 220°C (40 min). Injector and detector temperature were 240°C and 300°C, respectively. Column head pressure was 0.6 bar.

Oxychlordane and CTTs were enantioseparated on 20% *tert*.-butyldimethylsilylated β-cyclodextrin diluted in PS086 (β-BSCD), obtained from BGB Analytik (Adliswil, Switzerland); column parameters: 30 m × 0.25 i. d. × 0.18 μm d_f. Injector and detector temperature were 240°C and 350°C/270°C, column head pressure 1.0 bar. For the CTTs B8-1413 (Parlar #26) and B9-1679 (Parlar #50) substitute the following temperature program was used: 120°C (2 min), 15°C/min to 220°C (82 min), 20°C/min to 245°C (35 min). GC oven program for oxychlordane was as follows: 120°C (2 min), 15°C/min to 190°C (80 min), 20°C/min to 245°C (35 min). For confirmation of the enantiomeric ratios of oxychlordane, gas chromatography-electron ionization mass spectrometry GC-EIMS was performed on an HP 5989B MS Engine (Hewlett-Packard) connected to an HP 5890 II plus Series gas chromatograph (Hewlett-Packard). Both injector and transfer line temperatures were set at 250°C. The ion source and the quadrupole temperature were set at 200°C and 100°C, respectively. In the selected ion monitoring (SIM) mode, the characteristic masses for oxychlordane, i. e. m/z 385 and m/z 387, were detected. Samples were splitless (1.5 min) injected (250°C). Helium was used as carrier gas at 1.0 mL/min. A 25% β-BSCD

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column (BGB Analytik, Adliswil, Switzerland) was installed. The temperature program was 120°C (2 min), 15°C/min to 190°C (2 min), 2°C/min to 210°C (40 min), 10°C/min to 240°C (13.33 min). Total run time was 75 min.

RESULTS AND DISCUSSION

Composition of the Organochlorine Pattern in Livers of Icelandic Arctic Foxes

Figure 2 shows a typical GC-ECD chromatogram of the liver extract of an arctic fox from Borgarfjördur eystri (East Iceland). The organochlorine pattern was dominated by oxychlordane which is the principal metabolite of chlordane-related compounds.[15] This is contrary to ECD chromatograms of seal blubber from different locations around Iceland which are topped by p,p'-DDE.[3, 5] In livers of arctic foxes p,p'-DDE also reached the highest level of the DDT group, whereas p,p'-DDT was only lowly abundant and p,p'-DDD was not detected in any sample. The PCB congener pattern was dominated by PCB 180, followed by PCB 153 and PCB 170. PCB 138, PCB 163, PCB 99, PCB 194, and PCB 118 were identified as further major PCB congeners (see Table I). Levels of PCB 99 are missing in Table I since this major PCB congener in liver of arctic foxes (see

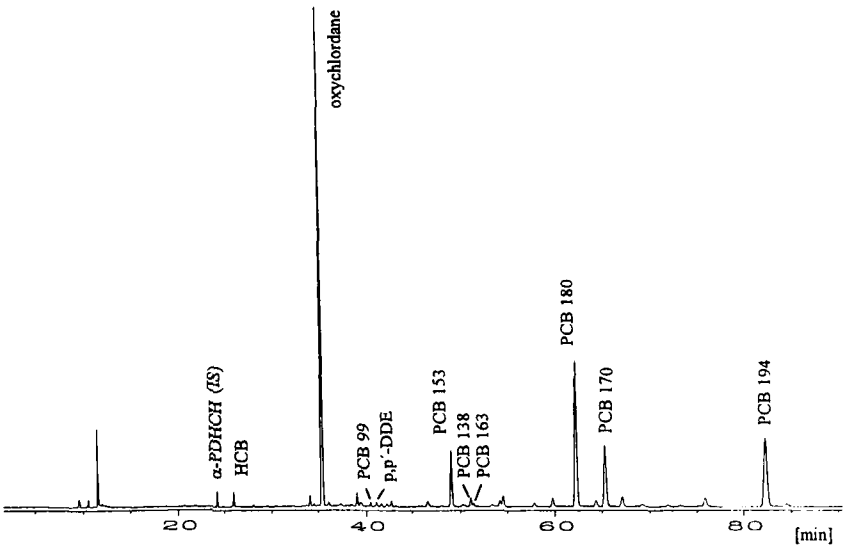

FIGURE 2 GC-ECD chromatogram (CP-Sil 2) of the liver extract of an arctic fox (Borgarfjördur, northeast coast of Iceland)

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TABLE I Organochlorine levels (μg/kg wet weight) in livers of polar foxes from Iceland and biological data of these animals

	Coast →						Interior →			
Sample	**P8**	**P9**	**P10**	**P11**	**P4**	**P5**	**P15**	**P3**	**P7**	**P6**
Sex	F	F	F	M	F	F	F	M	M	M
Age (month)	5	25	50	38	7	8	34	7	7	8
Date of catch	10/93	6/93	7/93	7/93	12/93	1/94	2/94	12/93	12/93	1/94
β-HCH	6	14	11	15	11	3	7	12	5	3
γ-HCH	3	5	5	2	11	4	4	11	4	5
HCB	26	31	111	71	6	1	3	7	1	<1
PCB 118	23	22	138	36	5	1	3	9	<1	1
PCB 153	194	235	2009	1346	28	19	17	45	11	7
PCB 138	31	32	190	129	6	4	<4	12	<4	<4
PCB 163	6	10	14	37	3	2	<2	3	<2	<2
PCB 180	337	493	3166	3015	21	20	34	42	18	7
PCB 170	59	78	1021	1308	6	4	8	10	4	2
PCB 194	21	77	1650	1723	<1	<1	7	6	<1	<1
p,p'-DDE	8	7	129	40	3	1	1	4	2	1
trans-nonachlor	27	8	74	61	3	2	<1	1	<1	<1
oxychlordane (nonchiral)	912	540	5308	7806	33	22	66	20	30	8
(+)-oxychlordane	560[1]	275[1]	2800[1]	3700[1]	22[2]	19[2]	39[2]	10[2]	17[2]	6[2]
(−)-oxychlordane	470[1]	190[1]	2300[1]	4650[1]	11[2]	10[2]	20[2]	7[2]	12[2]	4[2]
oxychlordane $ER_{(+/-)}$	1.2[1]	1.4[1]	1.2[1]	0.8[1]	2.0[2]	1.9[2]	2.0[2]	1.4[2]	1.4[2]	1.5

1) $ER_{(+/-)}$ determined on 20 % β-BSCD
2) $ER_{(+/-)}$ determined on β-TBDM

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Figure 2) was only available as qualitative standard. All other investigated PCBs were below the detection limit. The present PCB pattern is different to the PCB composition determined in most other species. This is due to both the investigated matrix (liver of arctic foxes) and the analytical method (stationary GC phase). Usually, PCBs without vicinal hydrocarbons, substituted at both para-positions are the most stable PCB congeners. Consequently, PCB 153, PCB 180, and PCB 194 should be very recalcitrant. Since PCB 153 is also a major congener in technical PCB mixtures, the PCB pattern of most warmblooded animals is dominated by this congener. PCB 153 also dominated the organochlorine pattern of two seal species from Iceland.[5] However, dominance of PCB 180 in the PCB pattern was also reported in adipose tissue and liver samples of arctic foxes from Svalbard[9] and adipose tissue of red foxes (*Canis vulpes*) in Germany.[16] The latter are morphicologically similar and close related to arctic foxes.[17] It was presumed that (arctic) foxes may have a cytochrome P-

450 isoenzyme that also metabolizes 2,4,5-substituted aromatic compounds similar to that of dogs.[16]

A second major PCB congener in seal blubber and technical PCB mixtures, PCB 138, was found only in low concentrations in the liver samples. On the other hand, PCB 163, which is only scarcely described in the literature had remarkable levels in most of the liver samples. This is due to coelution of PCB 138 and PCB 163 on the standard capillary columns for PCB separations i. e. DB5 (or SE-54, CP-Sil 8 and other similar phases) and OV-1701 (or CP-Sil 19 and other similar phases). Recently, some of us found that levels of PCB 163 were 15-65% in different technical PCB mixtures,[18] up to 30% in seal blubber,[11, 19] and >15% of PCB 138 in cod livers.[20] Application of the particularly nonpolar CP-Sil 2 column allowed a separate quantitation of PCB 163 and PCB 138 in the samples (see Figure 2 and Table I).

In addition to chlordane-related compounds we also screened for further organochlorine pesticides. Two major compounds of technical toxaphene, B8-1413 and B9-1679, were below the detection limit in all liver samples (see also below). HCH isomers and HCB are early eluted organochlorines. In the group of the hexachlorocyclohexanes only lindane (γ-HCH) and β-HCH were present while α-HCH was not detected in any sample. This was unexpected since α-HCH was abundant in seal blubber from Iceland[5] and also in air[21] and water from arctic regions.[22] To exclude loss of the very volatile α-HCH during sample preparation, we have applied perdeuterated α-HCH (α-PDHCH) as internal standard. α-PDHCH and α-HCH have the same properties in sample clean-up steps but are easily baseline separated by gas chromatography.[13] High recovery rates of α-PDHCH confirm that α-HCH was below the detection limit in the liver samples. A further early eluted organochlorine compound, HCB, was detected only in samples with high PCB levels (see Table I).

Regional Differences and Influence of Biological Parameters on Organochlorine Levels

The low sample size compared with the biological and spatial variables (sex, age, two locations) required very careful evaluation of the data. Nevertheless, significant differences in organochlorine levels of the two habitats were observed which merit presentation. The organochlorine pattern in samples from the coast was also typical of samples from the interior. However, organochlorine levels in samples from the interior were on average one order of magnitude lower than in juvenile arctic foxes from the coast and two orders of magnitude compared to adult samples from the coast (see Table II). Although five arctic foxes from the interior were younger than one year, there is no doubt that this population is less

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TABLE II Organochlorine levels (μg/kg wet weight) in liver and adipose tissue of a polar bear sampled north of Iceland

	Liver	Adipose tissue
α-HCH (nonchiral)	12	98
(+)-α-HCH[2]	9	59
(−)-α-HCH[2]	4	52
α-HCH $ER_{(+/-)}$[2]	2.2	1.1
β-HCH	16	84
γ-HCH	8	8
HCB	15	102
PCB 118	14	93
PCB 153	702	3861
PCB 138	168	667
PCB 163	99	223
PCB 180	458	1739
PCB 170	168	890
PCB 194	55	390
p,p′-DDD	161	n.d.
p,p′-DDE	109	678
trans-nonachlor	74	673
cis-nonachlor	n.d.	77
oxychlordane (nonchiral)	1685	816
(+)-oxychlordane[1]	1000	520
(−)-oxychlordane[1]	750	390
oxychlordane $ER_{(+/-)}$[1]	1.3 (1.4[2])	1.3 (1.2[2])
B8-1413 (Parlar #26)	n.d.	53
B8-1413 $ER_{(1/2)}$[1]	—	1.7
B9-1679 (Parlar #50)	n.d.	76
B9-1679 $ER_{(1/2)}$[1]	—	1.4

1) $ER_{(+/-)}$, $ER_{(1/2)}$ determined on 20% β-BSCD
2) $ER_{(+/-)}$ determined on β-TBDM n.d. = not detected

contaminated with organochlorines than the population at the coast. Independent of age and sex, the coastal sample with the lowest level of oxychlordane, PCBs or p,p′-DDE was much higher than the highest levels in the samples from the interior. These results are explicable with significantly different trophic levels of important prey species which are consumed by arctic foxes in coastal areas and inland habitats in Iceland. The arctic foxes from the coast are top predators of the marine food web.[9] A considerable proportion of the diet of coastal arctic foxes consists of prey items which belong to secondary or even tertiary consumers (e.g. fish eating birds, carcasses of seals etc.) while inland arctic foxes consume

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relatively more herbivorous prey species (e.g. ptarmigan *Lagopus mutus*, geese *Anser spp.*).[17] This difference has also been confirmed by analysis of stable carbon isotopes in Icelandic arctic foxes.[23]

In two liver samples from adult arctic foxes from the coast, particularly high PCB levels (>7 mg/kg) were obtained. These levels, based on liver wet weight, were even higher than PCB levels determined in blubber of seals from two locations in Iceland.[5] Therefore, the Icelandic arctic foxes from the coast must have grown up in a region with plenty of food. Arctic foxes from the interior feed on a lower trophic level of the terrestrial food web. In the coastal samples, the levels were higher in adult animals whilst this trend was not so pronounced in the samples from the interior. Wang-Andersen et al. also found high PCB levels in adult arctic foxes.[9] All in all, eating habits are likely to be the dominant factor leading to high organochlorine levels in arctic foxes.

PCB levels in Icelandic arctic foxes from the coast were on average higher, and those in samples from the interior lower than the average PCB levels in livers from Spitsbergen (approx. 0.4 μg/kg).[9] In former investigations some of us analyzed seal blubber from Iceland and Spitsbergen.[3] We found PCB levels twice as high in Iceland than in Spitsbergen. Thus, our results do not contradict the assumption that arctic foxes in Spitsbergen are members of the marine food web.[9]

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Enantioseparation of Oxychlordane and Further Organochlorines

As mentioned above the organochlorine pattern was dominated by oxychlordane. This metabolite of chlordane-related compounds is chiral, and enantioseparation of oxychlordane was recently described.[24] Furthermore, it was shown that several species accumulate different enantiomeric ratios of oxychlordane.[6, 14, 25-26] Recently, we enantioseparated oxychlordane and other organochlorine compounds on β-TBDM and β-BSCD.[14, 27] The elution order of the oxychlordane enantiomers was established by injection of enantioenriched (+)-oxychlordane. On β-BSCD (+)-oxychlordane eluted in front of (−)-oxychlordane and on β-TBDM the elution order was reversed. With that information we were able to define the oxychlordane enantiomeric ratio as quotient of the concentrations of (+)-oxychlordane to (−)-oxychlordane, abbreviated as $ER_{(+/-)}$. Usually, liver samples of arctic foxes showed higher levels of (+)-oxychlordane than (−)-oxychlordane, and the resulting $ER_{(+/-)}$ was up to 2.0 (see Table I). Surprisingly, the sample with the highest oxychlordane level showed an excess of (−)-oxychlordane and thus an $ER_{(+/-)} < 1$ (see Table I). This result, obtained

in the liver of an adult male arctic fox from the coast, was proven as follows. $ER_{(+/-)}$ were only calculated if the sum of the levels of the oxychlordane enantiomers deviated less than 15% of the oxychlordane level determined on the nonchiral column. Although this requirement was fulfilled in all investigated samples (see Table I) we additionally analyzed the samples by GC-EIMS in the SIM mode. For these experiments we applied a 25% β-BSCD phase (see Figure 3). With that method it is definite that the sample with the highest oxychlordane level had an $ER_{(+/-)} < 1$ which is different from all other samples from the same region.

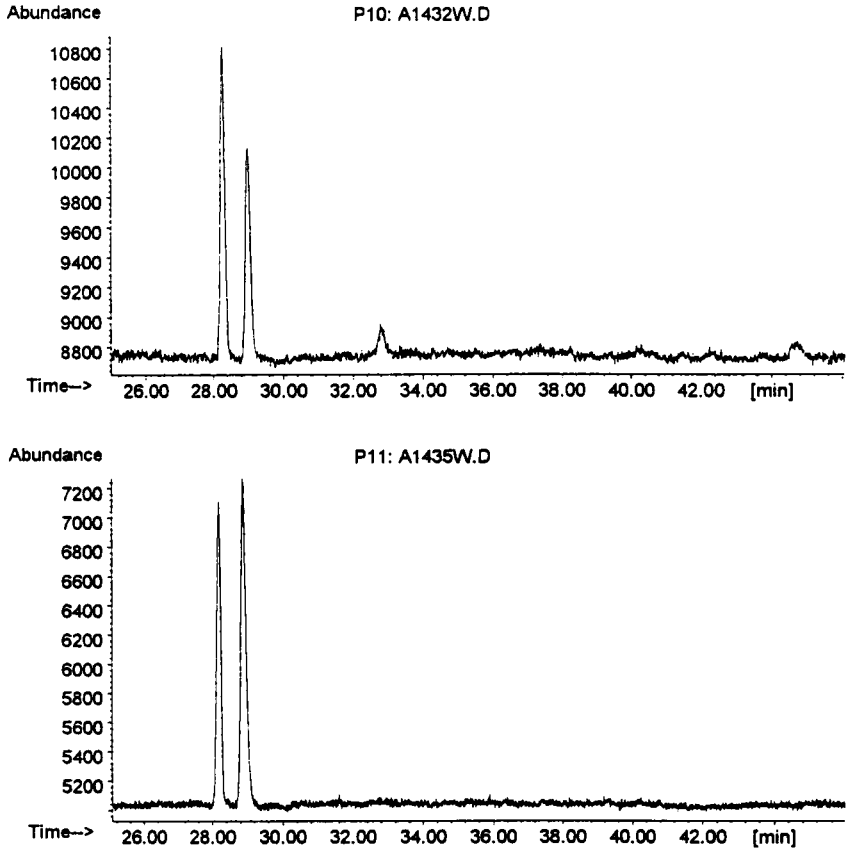

FIGURE 3 Enantioseparation of oxychlordane by GC-EIMS on 25% β-BSCD. (+)-oxychlordane eluted in front of (−)-oxychlordane above: sample P10 with enantioenriched (+)-oxychlordane below: sample P11 with enantioenriched (−)-oxychlordane

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Organochlorine Levels in Adipose Tissue and Liver of a Polar Bear Shot at the Icelandic Coast

Polar bears are not naturally occuring on Iceland. In some years pack ice drifts southwards to the coast of West-, North- and even East-Iceland. Under those circumstances polar bears sometimes reach the coast of Iceland. Since 890 AD at least 500 polar bears have been recorded.[28] The polar bears sighted on Iceland most probably belong to the East-Greenland-Spitsbergen population. Variations in the organochlorine pattern of subadult male polar bears were approx. one order of magnitude.[29] Therefore, the levels determined in the present sample should not be regarded as typical, especially since the polar bear also migrated to the territorial waters of Iceland.

Figure 4 shows GC-ECD chromatograms of extracts of liver and adipose tissue of the polar bear. The pattern is very different in these two tissues. The organochlorine pattern in the liver was similar to livers of arctic foxes. Oxychlordane was the predominant organochlorine compound, and PCBs and DDT and its metabolites were present in lower concentrations. Additionally, α-HCH was present in the liver of the polar bear. The organochlorine pattern of polar bear adipose tissue was dominated by PCB 153 followed by PCB 180 and oxychlordane.

The levels of the major congeners PCB 153, PCB 138, PCB 180, PCB 170, and PCB 194 were three to four times higher in adipose tissue than in the liver sample (see Table II). Norstrom et al.[15] reported that these PCB congeners and PCB 99 account for approximately 93% of the total PCB contents. PCB 99 was also identified as a major PCB congener in the samples (see Figure 4). The ratio of PCB 180 to PCB 153 was higher in liver than in adipose tissue, and this might be explained in the same way as for arctic foxes. Furthermore, the ratio of PCB

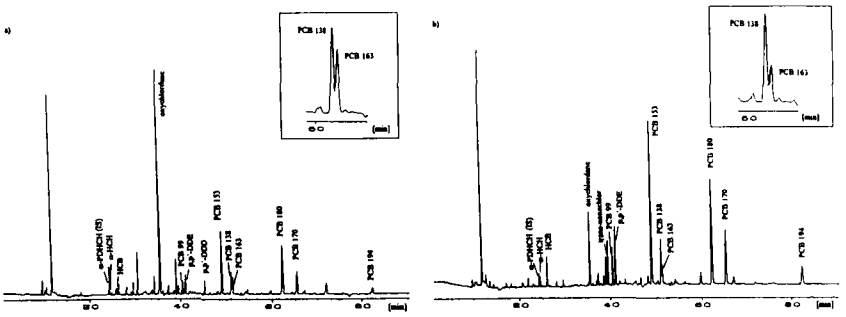

FIGURE 4 GC-ECD chromatograms (CP-Sil 2 column) of polar bear tissue sampled in the north of Iceland a) liver b) adipose tissue. Squares in the right corners show enlargement of the time range with the peaks of PCB 138 and PCB 163

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138 to 163 was also significantly different in liver and adipose tissue. PCB 163 reached 33% of PCB 138 in adipose tissue and almost 60% in the liver (see enlargements of Figure 4). It is noteworthy that Norstrom et al.[15] found that polar bears are more able to metabolize PCB 138 than seals. These authors reported identical levels of PCB 138 and PCB 170 in polar bears from the Canadian Arctic.[15] The level of PCB 170 in our sample was identical to the sum of PCB 163 and PCB 138 in adipose tissue. This demonstrates the importance of the separation of PCB 163 and PCB 138 for a proper congener specific PCB analysis. The ratios of the PCBs were very similar to those described in literature.[15, 29-30] This confirms that polar bears accumulate typical PCB patterns as well as the accuracy of our quantitation method. The simple PCB pattern in polar bears is accompanied with high levels of methylsulfone-PCB metabolites, which were approx. 9% of the parent compounds in liver and 3% in adipose tissue.[31]

Oxychlordane and p,p'-DDD were the only compounds more abundant in liver than in adipose tissue based on wet weight. In livers of polar bears from Svalbard, the level of PCB 153 was higher than the oxychlordane level.[29] Chlordane-related compounds were mostly applied in northern America. Due to the high oxychlordane level in adipose tissue, the polar bear may have migrated to Iceland from Greenland rather than Svalbard. An increase of the ratio of oxychlordane to PCB 153 ratio was reported from Svalbard to the Canadian arctic.[15, 29] The oxychlordane $ER_{(+/-)}$ was >1 in both liver and adipose tissue (see Table II).

In the DDT group, significant differences were observed in the tissues. The DDT level in liver was dominated by p,p'-DDD which was absent in the adipose tissue sample. Predominance of p,p'-DDD in livers was also observed in polar bears from the Canadian arctic.[15] The authors reported that post mortal degradation of DDT to DDD was expected to explain high DDD levels in the livers of dead animals.[15] In agreement with earlier findings, p,p'-DDE dominated the DDT pattern of adipose tissue of the polar bear.[15]

Compounds of technical toxaphene (CTTs) are further contaminants of arctic biota.[32] In blubber of seals and other mammals two CTTs, B8-1413 (Parlar #26) and B9-1679 (Parlar #50), are predominant and account for approx. 50% of the total CTT burden.[33] In the liver of the polar bear these two CTTs were not detected as it was observed in livers of arctic foxes (see above). In adipose tissue of the polar bear, however, both CTT congeners were present in low concentrations. CTTs elute in the same GC retention range as PCBs, and group separation is recommended for a proper quantitation even of the major CTTs.[20] This was not subject of this study. However, we have a further proof of the presence of the CTTs in the polar bear adipose tissue. Enantioseparation on

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β-BSCD gave two peaks for both compounds at the retention time of the standard mixture. This clearly confirms the presence of the CTTs in the samples. α-HCH, β-HCH, and γ-HCH were present in both tissues of polar bear. High levels of β-HCH and α-HCH were determined, particularly in adipose tissue. This is different from the arctic foxes who had no α-HCH in measurable concentrations. We have also enantioseparated α-HCH and found a stronger enantioselective enrichment in the liver than in adipose tissue (see Table II). In both tissues (+)-α-HCH was more abundant which was also observed for harbour seals (*Phoca vitulina*) and grey seals (*Halichoerus grypus*) but not in hooded seals (*Cystophory cristata*).[34]

CONCLUSIONS

Arctic foxes in Iceland are highly polluted and organochlorine levels are strongly dependent on the food reservoir. A concrete evaluation of the detected organochlorine levels is only possible when it is known whether a population is a member of the marine or the terrestrial food web. Origin of polar bears on Iceland may be distinguished by the oxychlordane level. High levels of oxychlordane relative to PCBs point to migration from the west (Greenland), lower oxychlordane levels to the east (Svalbard).

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