Chlorinated paraffins in fishes and seabirds from northwest Europe and the Arctic island Bjørnøya

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Introduction

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated *n*-alkanes containing thousands of different isomers. They are divided according to their carbon chain length into short chain CPs (SCCPs, C_{10}-C_{13}), medium chain CPs (MCCPs, C_{14}-C_{17}) and long chain CPs (LCCPs, $C_{>17}$). The degree of chlorination can vary between 30 and 70%. CPs are mainly utilized as additives in metal working fluids, as flame retardants and as plasticizers [1].

The analysis of CPs is time-consuming and complex. Information about environmental levels is currently scarce compared to other persistent organic pollutants (POPs) such as polychlorinated biphenyls and toxaphenes, although CPs have similar chemical and physical properties. CPs are classified as persistent, do bioaccumulate, and are toxic to aquatic organisms [1].

Long range atmospheric transport of SCCPs and their presence in sediments and marine mammals from the Canadian Arctic was shown by Tomy et al. [2, 3]. However, there are almost no data from the European Arctic. The Arctic island Bjørnøya (Bear Island), although 500 km away from any known source point, is known for high concentrations of POPs. Especially, Lake Ellasjøen on Bear Island is contaminated due to two reasons: Large seabird colonies are located at the lake and the input of guano causes an increase in POP levels. Moreover, the lake area is mountainous and receives a lot of precipitation and thus more airborne contaminants than many other Arctic areas [4].

In this study fish and seabirds from Northern Europe and the Bear Island were analyzed for SCCPs and MCCPs by high resolution gas chromatography (HRGC) coupled to low resolution mass spectrometry (LRMS) in the electron capture negative ionization (ECNI) mode. Special attention was focused on the investigation of changes of the pattern of congener and homologue groups.

Methods and Materials

Fish and seabird samples. Six cod liver samples (*Gadus morhua*) were obtained from the Norwegian Institute for Air Research in Tromsø. Two cods were caught close to the Northern Norwegian coast (Lofoten), two south of Iceland (Vestmannaeyjar) and two north of Iceland (Akureyri). Samples from Bear Island were provided by Akvaplan-niva (Tromsø, Norway). Two Arctic chars (*Salvelinus alpinus*) were caught in Lake Ellasjøen. Two little auks (*Alle alle*) and two kittiwakes (*Rissa tridactyla*) were shot at Bjørnøya. Liver and muscle tissues were analysed. More detailed information is given in Table 1.

Experimental details. Information about standards, chemicals, clean-up, quality control, instrumentation, and quantification, are published in detail elsewhere and therefore only briefly described [5-7]. Samples were homogenized with a tenfold excess of anhydrous sodium sulphate. 10 ng of $^{13}C_{10}$-*trans*-chlordane (internal standard, purity 99%, Cambridge Isotope Laboratories, USA) in 10 µl of cyclohexane were added and the sample extracted with 250 ml of *n*-hexane/CH_2Cl_2 (1+1, v/v) in a glass column. After concentration, lipids were removed by column chromatography on 40 g of silica gel impregnated with 44% (weight) of conc. H_2SO_4. The lipid-free sample was eluted with 120 ml of *n*-hexane/CH_2Cl_2 (1+1, v/v). A further fractionation was carried out on 16 g of Florisil® (1.5%

water content) with 85 ml of *n*-hexane (fraction 1), 5 ml of CH_2Cl_2 (fraction 2) and 65 ml of CH_2Cl_2 (fraction 3). The last fraction contained all CPs. 10 ng of ε-hexachlorocyclohexane (ε-HCH, Ehrenstorfer, Germany) in 10 µl of cyclohexane were added as recovery standard to the concentrated CP fraction before analysis.

Chromatographic separations were performed on an HP 5890II (Hewlett Packard, USA) gas chromatograph equipped with a split/splitless injector and a fused silica capillary column (15 m, 0.25 mm i.d.) coated with a 0.25 µm thick film of DB5-MS (5% phenyl-methylpolysiloxane, J&W Scientific, USA). The temperature programme was as follows: 100 °C, isothermal for 2 min, then 15 °C/min to 280 °C and isothermal for 8 min. An HP 5989B (Hewlett Packard, USA) mass spectrometer was employed in the ECNI mode using methane (99.995%, Carbagas, Switzerland) as reagent gas. The most abundant isotopes of the $[M\text{-}Cl]^-$ ions of CPs (quantification and confirmation ion) were detected in the selected ion monitoring (SIM) mode. For quantification three SCCP standards and two MCCP standards were used for the establishment of the linearity function (51%, 55%, 63%, 52% and 57% Cl, 100% purity, Ehrenstorfer, Germany). Response factors of CPs in the samples were determined by the calculated chlorine contents of the samples and the linearity of the standard mixtures [7].

Results and Discussion

CP concentrations. CPs were detected in all analyzed samples. Concentrations of SCCPs and MCCPs were in a similar range (see Table 1). Calculated on lipid weight basis the S+MCCP concentrations were higher in the samples from Bear Island. CP concentrations were detected in both muscle and liver of each species from Bear Island, but concentrations in the tissues varied and no trend was observable.

Table 1: SCCP and MCCP concentrations (ng/g wet weight) determined by HRGC-ECNI-LRMS in fish and seabirds from Northern Europe.

Species	Gender	Origin	Sampling date	Lipid [%]	Concentration [ng/g ww]	
					SCCPs	MCCPs
Cod (L)	f	Norway, Lofoten[1]	02.02.04	37	52	47
Cod (L)	f	Norway, Lofoten[1]	02.02.04	49	17	7
Cod (L)	f	North of Iceland[2]	30.09.03	47	56	16
Cod (L)	f	North of Iceland[2]	30.09.03	39	11	7
Cod (L)	n.d.	South of Iceland[3]	06.11.03	51	52	18
Cod (L)	f	South of Iceland[3]	06.11.03	49	70	47
Arctic char (L)	f	Bear Island[4]	09.07.01	12	27	43
(M)				2	13	47
Arctic char (L)	f	Bear Island[4]	09.07.01	12	11	13
(M)				2	7	10
Little auk (L)	m	Bear Island[4]	08.07.01	10	18	48
(M)				5	7	55
Little auk (L)	m	Bear Island[4]	08.07.01	10	88	371
(M)				4	16	17
Kittiwake (L)	m	Bear Island[4]	08.07.01	5	6	39
(M)				5	5	38
Kittiwake (L)	f	Bear Island[4]	08.07.01	6	44	12
(M)				12	5	5

L: liver; M: muscle; ww: wet weight; n.d. not determined; 1: 68°08'N/13°33'W; 2: 65°74'N/18°09'W; 3: 63°28'N/20°15'W; 4: 74°N,19°E, Lake Ellasjøen

Congener group patterns. Considerable differences in the congener group patterns were observed (see Figure 1). The high abundance of congener groups with ten carbon atoms is consistent with their higher vapor pressures and may indicate long-range atmospheric transport. However, also highly chlorinated CPs were present, which suggests that the CP patterns in the organisms are

a result of exposure to long-range atmospheric transported CPs and bioaccumulation and biomagnification processes.

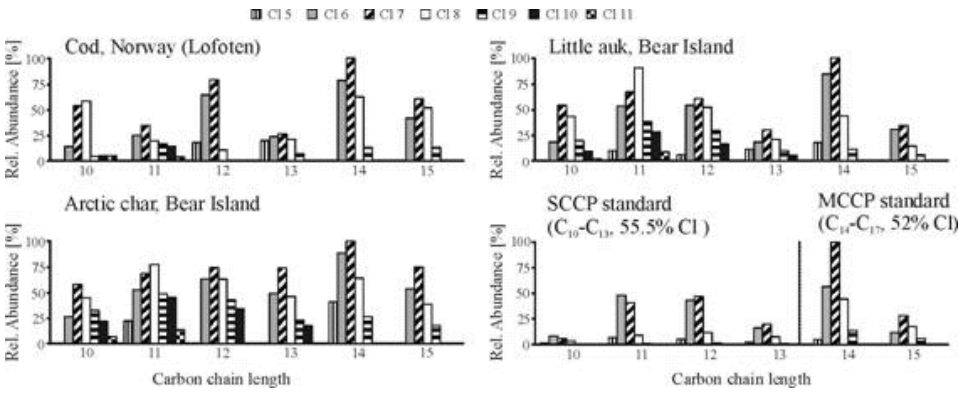

Figure 1: Congener group patterns of a cod sample from Norway (Lofoten), an Arctic char, a little auk sample from the Bear Island and two standard mixtures (SCCPs, 55% Cl and MCCPs 52% Cl).

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