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Persistent organic pollutant content in cod (*Gadus morhua* L.) from the Barents Sea region

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Abstract

The aim of this study was to examine levels of **persistent organic pollutants** (POPs) in cod from the Barents Sea. Samples were collected in two regions, the warm waters of the West Spitsbergen Current, where surface temperatures are typically 3.5-6.5°C, and the cold waters of the East Spitsbergen Current, where the surface temperature is generally –1.5-1.5°C.

The concentrations of selected POPs were analysed in muscle and liver tissues of cod. The observed POPs content were lower than in comparable samples from urban regions. Significant differences were seen between the POPs contents in samples of cod from the two regions. These differences can be attributed to the distinct characteristics of the two water bodies, the West and East Spitsbergen Currents.

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INTRODUCTION

Persistent organic pollutants (POPs) are a class of chemicals that cause significant concern due to their environmental persistency and their continuing use in developing countries. POPs are global contaminants and are ubiquitous, being found even in remote areas far from emission sources. Global distribution patterns have been extensively documented (Barrie 1986; De Voogt and Jansson 1993; Oehme and Manö 1984; Risebrough et al. 1976; Tanabe et al. 1983; Villa et al. 2003; Wania and Mackay 1993, 1996). It is generally assumed that the degradation of volatile and semi volatile compounds is slower in colder areas than warmer ones, since biodegradation and volatilisation processes are known to be temperature dependent (Bignert et al. 1998). As temperature decreases, biodegradation slows down, and air/water concentration ratio decreases, causing a lower rate of removal by photolysis in air. However, recent Swedish data indicate that the levels of many polychlorinated organic compounds (POCs) decrease at similar rates in the Subarctic and locally polluted areas in the southern Baltic Sea (Bignert et al. 1998, Olsson et al. 1998).

Since the late 1960s, detectable concentrations of POPs have been discovered in many environmental matrices (air, water, sediments, and biota) in Antarctica and the Arctic (Macdonald et al. 2000, Muir et al. 1995, Risebrough et al. 1976, Sladen et al. 1966, Tanabe and Tatsukawa 1980).

The Barents Sea is part of the Arctic Ocean located north of Norway and Russia. It is a rather deep shelf sea (average depth 230 m), bordered by the shelf edge of the Norwegian Sea to the west, the island of Spitsbergen (Svalbard) to the northwest, and the islands of Franz Josef Land and Novaya Zemlya to the northeast and east. There are two main water masses in the Barents Sea, the warm West Spitsbergen Current, from the North Atlantic Drift, and the cold East Spitsbergen Current, from Arctic water. The West Spitsbergen Current runs south - north across the Barents Sea, Greenland Sea and along the western coast of Spitsbergen. The temperature of the surface water in this region is 3.5-6.5°C (salinity >35 PSU). The East Spitsbergen Current runs north - south and the temperature of surface water in the winter is below -1.5°C (salinity 34.3 – 34.8 PSU) and rises in the summer to 0.1-1.5°C (salinity 31.0-34.2 PSU). The physiochemical properties and geographical extents of the two currents are variable on short-term, inter-annual and longer term scales (Ferdynus 1997, Haugan 1999, Jones 2001, Loeng 1991, Løyning 2001, Midttun 1990, Mitchell et al. 1991, Proshutinsky et al. 1999, Styszyńska and Wiśniewska 2002). Studies carried out in the regions of Spitsbergen and Franz Josef Land indicate significant physiochemical differences within the water bodies, both vertically and horizontally (Lydersen et al. 2004). Vertically there are three main types of water mass, cold surface water (to 200 m depth), warm Atlantic water (200-900 m depth) and cold near-bottom water (from 900 m to the bottom) (Løyning 2001, Midttun 1990, O'Dwyer et al. 2001).

The Atlantic cod (*Gadus morhua* L.) is a well-known foodfish belonging to the family Gadidae. Its habitat ranges from the shoreline down to the continental shelf. In the western Atlantic Ocean cod is distributed north of Cape Hatteras, North Carolina, and round both coasts of Greenland. In the eastern Atlantic it is found in the Bay of Biscay, the north Atlantic, including the North Sea, around Iceland and in the Barents Sea, which is its most important feeding area.

Cod populations differ both in appearance and biology, depending on their local environment. Atlantic cod can adapt to differences in water salinity and temperature, but usually prefer temperatures of 0-7°C (optimum temp. 4°C). Young fish endure temperatures as low as -1.3°C, with sensitivity to the cold increasing with age. The cod population from the Barents Sea (fish 3 years and older) spawn in March and April along the Norwegian coast in the region of Lofoten; in summer they reach the Barents Sea. The direction of feeding migrations of these adult cod is similar to the North Cap Stream direction, and they generally return by the same route (Demel and Rutkowicz 1958, Ottera et al. 1999, Pęczalska 1981, Rutkowicz 1982, Stensholt 2001).

This study was undertaken in order to examine POPs in the muscle and liver tissues of cod from the Barents Sea in an effort to disclose the levels of contamination, and geographical variations in the distribution of these chemicals, in the different water bodies of that area.

MATERIALS AND METHODS

Sample collection

Samples were collected from two sites in the Barents Sea (Fig. 1). The temperature of surface water (basing on maps from the NOAA-CIRES Climate Diagnostics Centre) at Station 1 (near Bear Island) was 4.5-5°C, this area being under the influence of the warm West Spitsbergen Current. Station 2 (SE Spitsbergen) was located in an area under the influence of the cold East Spitsbergen Current, and correspondingly had a surface temperature of -1.5°C (Fig. 1).

Cod were caught during a cruise of m/v HINOPLEN by a trawl net at a depth of 300 m. The analysed fish (n = 12 from each station) were 50-60 cm long (6-7 years old). Muscle and liver tissue were collected for further analyses, attention being paid to collect liver tissue free of parasites.

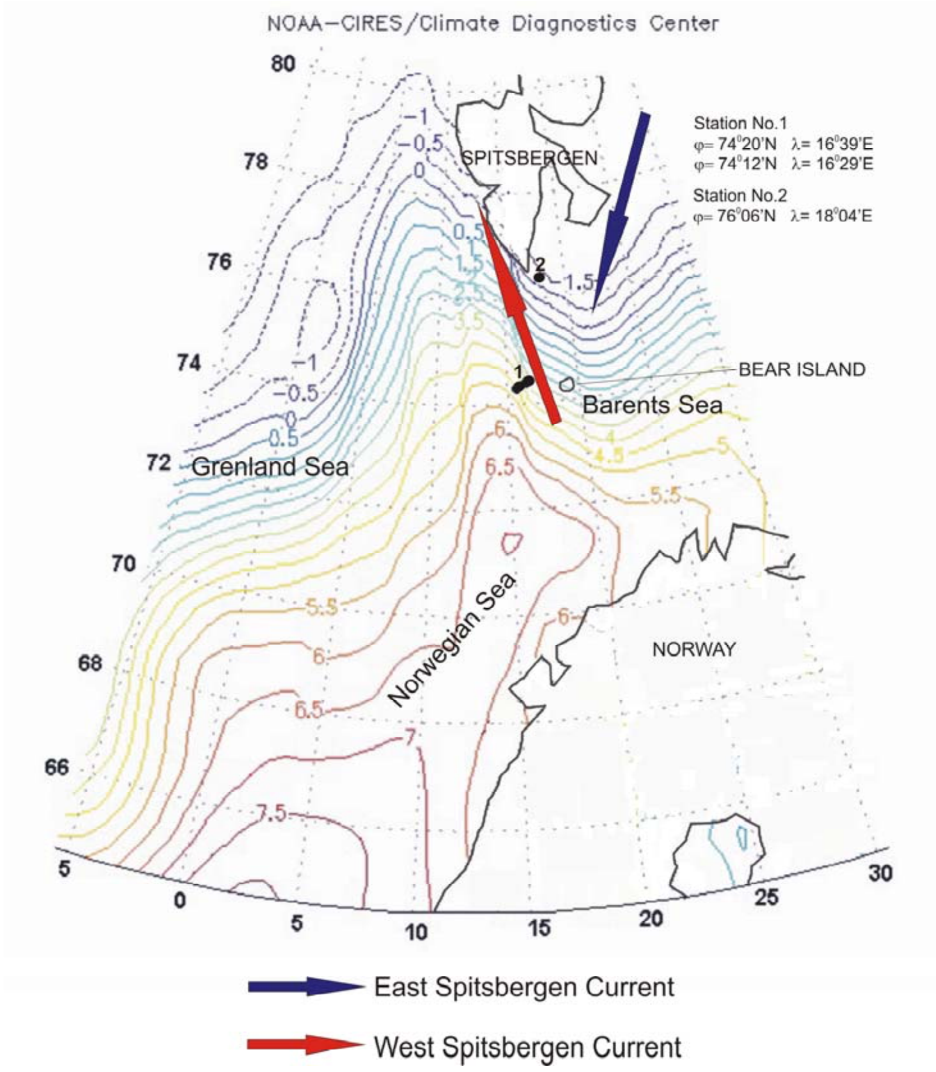

Fig. 1. Map showing location of sampling stations and temperature of surface water.

Organochlorine analysis and lipid content determination

The fish muscle and liver samples were weighed and freeze-dried. Each sample was then homogenised, weighed again, and transferred to a glass vial for extraction with acetone and *n*-hexane (20:12 v/v) in a modified Soxhlet apparatus, for 3 h. A sub-sample of the extract was used to determine the fat content gravimetrically. After extraction, water was added to separate the acetone and polar impurities. Concentrated H_2SO_4 (96%) was added to oxidise the fat. The hexane fraction was evaporated in a vacuum centrifuge to dryness (Bremle et al. 1995, Sapota 1997).

An open column step was performed to clean the samples. A column was prepared by adding 4 cm^3 of activated silica gel soaked with 1 g of concentrated H_2SO_4 (99%) to 18 cm^3 of elution liquid (*n*-hexane:dichloromethane (95:5 v/v)) in a glass column. When the gel had sedimented, 4 cm^3 of silica gel soaked with 1 cm^3 of 1 M K_2CO_3 was added. The alkaline gel adsorbed acidic substances (e.g. fatty acids) and the oxidised acidic gel retained non-persistent compounds. The samples were redissolved in *n*-hexane and transferred to the silica gel column. 3 cm^3 of elution liquid was added and the elute was discarded. The elute from the next additions of 5 cm^3 and 10 cm^3 elution liquid was collected. The elutes were placed in a vacuum centrifuge and the solvent evaporated after which 0.4 cm^3 of *iso*-octane was added. A mixture of pesticides containing *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, α, β and γ-HCH, HCB and a PCBs mixture containing seven congeners (28, 52, 101, 118, 138, 153, 180) were used as standards. Samples were analysed by capillary gas chromatography with electron capture detector (ECD) in a VARIAN STAR 3400 equipped with a split-splitless injector and an autosampler. The POPs were separated on a 30 m DB 5 quartz capillary column with H_2 as a carrier gas and N_2 as a make-up gas (Bremle et al. 1995, Sapota 1997). Limits of detection (LoD) were calculated as the concentration of analysed substances in the carrier gas which gave a signal of twice the noise level (Rödel and Wölm 1982). The LoD of HCH isomers and HCB was 1 ng g^{-1}. The LoD of DDT and its metabolites and PCBs was 10 ng g^{-1}.

RESULTS AND DISCUSSION

Concentrations of lipids and almost all of the analysed POPs were significantly higher in the muscle tissues of cod from Station 1 (warm water mass) than those from Station 2 cold water mass) (Table 1, figs. 2a, b and 3). High POPs content is associated with high lipid content because persistent organic pollutants are typically lipophilic (and therefore bioaccumulative). The average lipid contents were 1.23% of wet weight (SD ±0.29) in muscle samples from Station 1 and 0.91% of wet weight (SD ±0.12) in muscle samples from Station 2. The differences in POPs and lipid contents of the liver samples between the two sites were less marked than those of the muscle samples (Figs. 4a, b and 5). The average lipid contents in cod livers were 55.36% of wet weight (SD ±10.47) in samples from Station 1 and 49.76% of wet weight

Table 1

Comparison of POPs content (ng g^{-1} per lipid weight) in various fish species

Species	Sample origin and year	Analysed tissue	Σ HCH	ΣDDT	Σ_7PCBs	References
Gadus morhua – Station 1	Barents Sea, near Bear Island (2002)	muscle tissue liver	2 6	134 59	214 94	this study
Gadus morhua – Station 1	Barents Sea, near Bear Island (2002)	muscle tissue liver	2 6	134 59	214 94	this study
– Station 2	Barents Sea, SE Spitsbergen (2002)	muscle tissue liver	0.5 3	51 49	85 84	this study
Gadus morhua	southern Baltic Proper (1989)	liver	580	6300	3663	Falandysz et al. 1994a, b
Gadus morhua	North Sea (1982)	liver	66	1700	1846	Falandysz et al. 1994a, b
Gadus morhua	Norwegian Sea (1983)	liver	160	1400	2032	Falandysz et al. 1994a, b
Gadus morhua	North Atlantic (1984)	liver	72	860	795	Falandysz et al. 1994a, b
Gadus callarias	Vestertana Fjord (1993)	liver	16	112	224	Sinkkonen and Paasivirta 2000
Gadus callarias	Vestertana Fjord (1998)	liver	8	54	104	Sinkkonen and Paasivirta 2000
Zoarces viviparus	Gulf of Gdańsk (1997)	muscle tissue	8	311	717	Sapota 2004a
Myoxocephalus scorpius	Gulf of Gdańsk (1997)	muscle tissue	118	528	1917	Sapota 2004a
Salmo trutta	Gulf of Gdańsk – mouth of Vistula (1996)	muscle tissue	98	3330	2443	Sapota 2004a
Clupea harengus	southern Baltic Proper (2002)	muscle tissue	13	338	452	Sapota 2004b

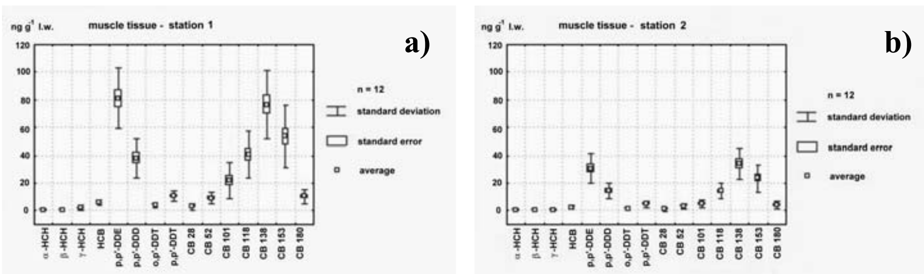

Fig. 2. Concentration of investigated POPs in muscle tissue of cod from Station 1 (a) and Station 2 (b).

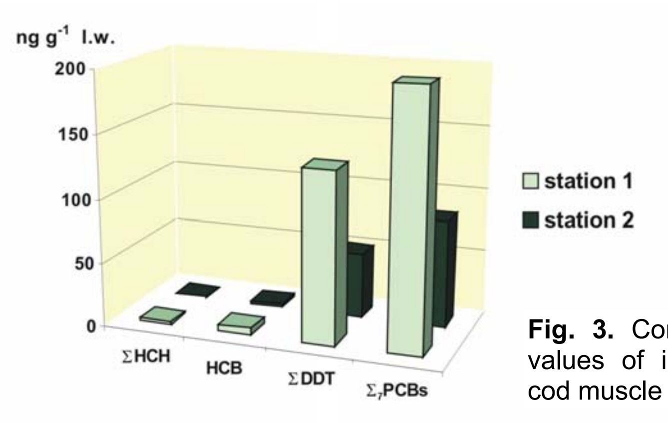

Fig. 3. Comparison of average values of investigated POPs in cod muscle tissue.

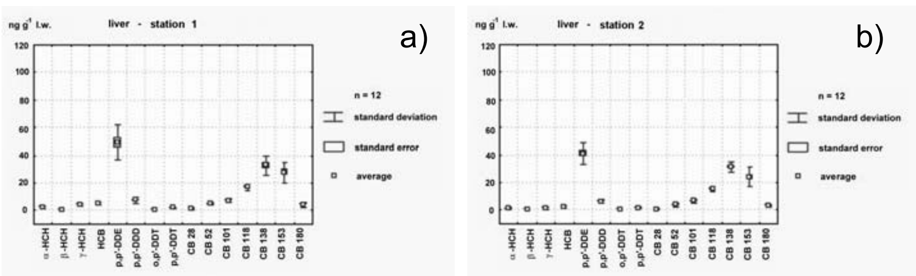

Fig. 4. Concentration of investigated POPs in cod liver from Station 1 (a) and Station 2 (b).

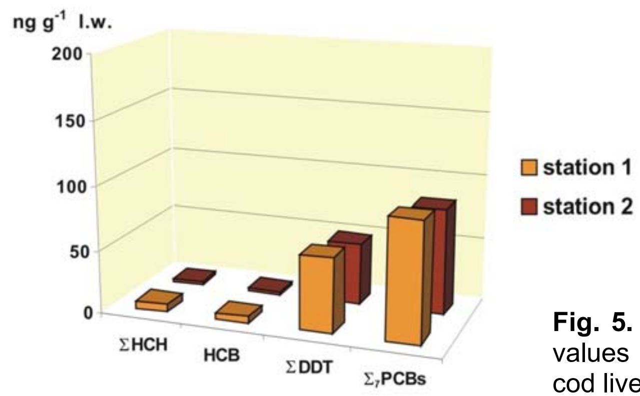

Fig. 5. Comparison of average values of investigated POPs in cod liver.

(SD ±5.70) in samples from Station 2. The highest POPs concentrations were observed in the muscle tissues of cod from Station 1 (Figs. 2a, b and 3). The POPs concentrations in muscle and liver samples from Station 2 were comparable, both being lower than those at Station 1.

A comparison of POPs content in various fish species from the Baltic Sea and Arctic regions is shown in Table 1. The POPs concentrations identified in cod in this study were significantly lower than in cod from the Baltic Sea. Contents of investigated substances of liver samples from Station 1 similar to concentrations observed in *G. callarias* liver samples from Vestertana Fjord (Sinkkonen and Paasivirta 2000). Falandysz et al. (1994a, b) reported higher concentrations of POPs in cod liver samples from the Baltic Sea, the Norwegian Sea, the North Sea and the North Atlantic than those observed in this study.

The concentrations of α and β-HCH in all muscle tissue samples, and the concentrations of β-HCH in liver samples from Station 2, were below the LoD. A very low concentration of β-HCH (average value 0.07 ng g^{-1} lipid weight) was seen in liver samples from Station 1. In the Arctic (for example the Bering Sea), gas exchange with the ocean or washout by rain can provide a mechanism to remove β-HCH selectively from the air as it moves northward, simply due to its exceptionally low HLC (Henry's Law constant) (Li et al. 2002).

HCHs were the most abundant POPs observed in the Arctic atmosphere and surface water (Li et al. 1998). Significant drops in the concentrations of α-HCH in the Arctic atmosphere were observed from 1982 to 1983 and from 1990 to 1992 (Bidelman et al. 1995, Jantunen and Bidelman 1995, Li et al. 1998). Further, in southern Norway during the five year period from 1991 to 1995 a 50% decline was observed in atmospheric concentrations of α-HCH, but not of γ-HCH (Haugen et al. 1998).

The concentrations of HCB in analysed fish were higher in samples from Station 1 than Station 2 (in both muscle tissue and liver) (Figs. 2a, b and 4a, b). HCB has been used as a fungicide and as an ingredient in the production of chlorinated solvents, as well as being formed as a by-product in various industrial processes (Barrie et al. 1992). Time-trend data from the Baltic Sea showed a very slow decrease in HCB levels and suggested the possibility of continued input, or a very slow clearance rate, of this compound in the marine environment (Kannan et al. 1992). High levels of HCB have been reported in liver samples of cod from the North Atlantic (Falandysz et al. 1994a) and the North Sea (de Boer 1989). The cod liver is rich in fat and used for production of cod liver oil, which is an important product in the pharmaceutical industry as well as in the human diet.

In all samples analysed (muscle tissue and liver) *p,p'*-DDE was dominant among DDT and its metabolites (Figs. 2a, b and 4a, b). DDT and its metabolites were reported as the organochlorine insecticides present in the highest concentrations in cod liver oil from all geographical locations studied (Falandysz et al. 1994a), their concentrations decreasing geographically: southern Baltic > western Baltic > North Sea > Norwegian Sea > Shelf of Iceland > Northwest Atlantic. Cod liver samples from Vestertana Fjord, on the Arctic coast of Norway, in the period 1983-1993 indicated a significant decrease in DDT concentrations, but not of its metabolites DDE and DDD (Sinkkonen and Paasivirta 2000).

The total content of seven polychlorinated biphenyls was higher in muscle samples of cod from Station 1 than Station 2 (Figs. 3 and 5). The concentrations of PCBs in cod from Station 2 were comparable in muscle tissue and liver samples. Of the analysed PCBs, CB138 and CB153 were dominant. Recent investigations of temporal declines in PCB levels in cod liver oil from the southern Baltic Sea have showed a very slow reduction, with concentrations exceeding 7 $\mu g\ g^{-1}$ lipid weight even in the late 1980s (Kannan et al. 1992). The presence of high concentrations of PCB isomers in cod livers from the southern Baltic Sea suggest the possibility of ongoing PCBs contamination and/or slow clearance of PCBs in that ecosystem (Falandysz et al. 1994b). CB138 and CB153 are the most prominent of the many PCBs present in biota (Falandysz et al. 1998a, b, c; Lee et al. 1996a, b). Cod liver oils collected from fish from other parts of the Baltic Sea, such as the Gulf of Finland (Kostinen 1990) and the Karlskrona archipelago (Asplund et al. 1990), reportedly contain relatively lower concentrations of non-*ortho* coplanar PCBs. Cod from the Arctic coast of Norway were much less contaminated (Kostinen et al. 1989).

The observed distributions of the investigated POPs in cod muscle tissue were similar in the samples from both Stations (Fig. 6a and b). This pattern,

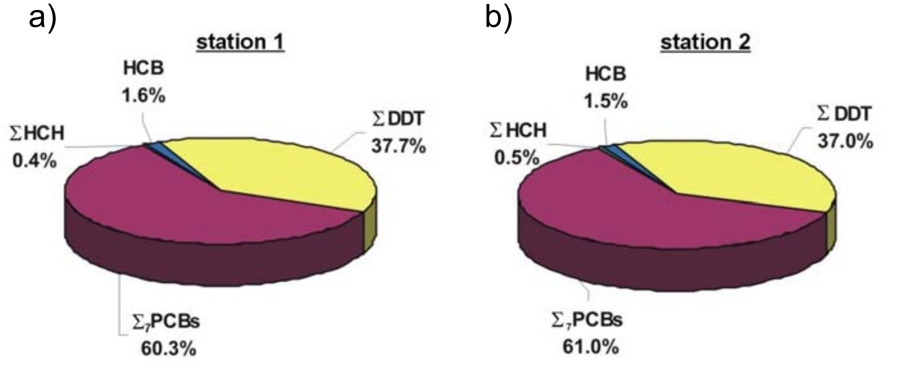

Fig. 6. Distribution pattern (%) of investigated POPs in muscle tissue of cod from Station 1 (a) and Station 2 (b).

with PCBs predominant is characteristic of benthic organisms and bottom feeding fish (Sapota 2002).

The differences in POPs contents of the studied samples probably result from differences in the water masses in which the fish live. It seems that the cod populations migrate with water mass and so, depending on marine current activity, can appear in the same geographical region but at different times of the year. It cannot be excluded that some groups of fish can associate with warm or cold water masses to which they return following spawning. Migratory species, including whales, fish and birds, can impact on the location of contaminants by obtaining contaminant loading in one location and subsequently releasing it in another. Migrating animals can also be subject to varied exposure as they feed along their migration paths (AMAP 2003).

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