

Article

Persistent Organic Pollutants (POPs) in Fish Consumed by the Indigenous Peoples from Nenets Autonomous Okrug

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Abstract: Currently, monitoring of persistent organic pollutant (POP) content in various biological and environmental matrixes in the Arctic is an urgent task. The present study focused on the determination of POPs such as: PCB#28, PCB#52, PCB#101, PCB#105, PCB#118, PCB#123, PCB#153, PCB#128, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, hexachlorobenzene (HCB), cis-nonachlor, trans-nonachlor, cis-chlordane, trans-chlordane, mirex, 1,2,3,5-tetrachlorobenzene and 1,2,4,5-tetrachlorobenzene in fish consumed by the indigenous people of the Nenets Autonomous Okrug (NAO) of the Russian Arctic. Fish samples were analyzed by gas chromatography triple quadrupole mass spectrometry (GC-MS/MS) using the multiple reaction monitoring (MRM) technique. The obtained results show that the major POPs in fish were dichlorodiphenyltrichloroethane (DDT) breakdown products and polychlorinated biphenyls (PCB) congeners. The $\sum\text{PCB}_8$ in pink salmon, Arctic char, navaga, humpback whitefish and northern pike were 1.54, 1.58, 1.24, 0.72 and 0.32 ng/g (ww), respectively. The main PCB congeners maximum average medium concentrations were 0.68 ng/g (ww) and 0.51 ng/g (ww) of PCB#153 in navaga and PCB#128 in pink salmon, respectively. The main DDT breakdown product was p,p'-DDE. In Arctic char, pink salmon, navaga, humpback whitefish and northern pike, the concentration of p,p'-DDE was 0.58, 1.61, 0.49, 0.63 and 0.08 ng/g (ww), respectively. A moderate positive relationship between $\sum\text{PCB}_8$ and lipid content and a high positive relationship between $\sum\text{DDT}$ and lipid content were observed. In fish samples with fat content <0.5% (northern pike, humpback whitefish), the amount of analyzed POPs was 2 or more times lower than that in fish species with fat content >1% (pink salmon, Arctic char). Despite the large number of fish in the diet of indigenous peoples from NAO, no significant risks were identified. Most legacy POP and organochlorine pesticides (OCPs) tend to decrease, which can be explained by past national and regional bans and restriction on their use and emission.

Keywords: persistent organic pollutants (POPs); PCB congeners; DDT; GC-MS/MS; fish; Russian Arctic; biomonitoring

1. Introduction

The Arctic region is considered to be one of the few unspoiled ecosystems; however, it is also subjected to the negative impact of persistent organic and inorganic pollutants (POPs and PIPs) through transboundary transfers, and to a lesser extent, via ocean currents and rivers [1,2]. Due to physicochemical properties, POPs and mercury (Hg) typically bioaccumulate and biomagnify in organisms, especially in fat tissues in aqueous food webs in the Arctic.

These environmental chemical pollutants have been shown to cause negative effects on human health [3–5], such as diseases of liver and cardiovascular systems, damage to organs and tissues and endocrine disorders with consequences for the reproductive system [6]. They cause teratogenic effects (birth defects), neurodevelopmental disorders and subclinical brain dysfunction. During early fetal development, exposure to Hg, PCBs and pesticides can cause brain damage at doses much lower than those affecting adult brain function [7,8].

To date, there is lack of knowledge about POPs and PIPs related risks in Russia and in the Russian Arctic in particular, which is highlighted in many international reports prepared as part of the Global Monitoring Plan and AMAP initiative [9].

Indigenous populations in the Russian Arctic are at greater risk of potentially adverse health outcomes [10,11]. Approximately 30–35% of the indigenous diet is fish such as pink salmon, Arctic char, navaga, humpback whitefish and northern pike. Fish can accumulate high amounts of POPs and Hg, and this is one of the sources of their entry in human organism [12,13]. These data differ from the average for Russia, where it is 26% [14]. POPs stay longer in the Arctic environment due to the low annual temperatures. It increases the possibility of getting them into local hydrobionts used in food [15–17]. The exposure to persistent toxic substances through traditional food is one of the main risk factors for human health in the Arctic [8]. The concentrations of some key Legacy POPs listed in the Stockholm Convention have declined in marine biota in other Arctic regions during the past two decades. Conversely, the concentrations of polychlorinated biphenyls (PCBs) and chlordanes have remained relatively constant and at high amounts in wildlife [18].

The quality of locally collected freshwater and marine seafood in the indigenous peoples' diet is not controlled by the Russian state, as these products do not enter the market. Migratory fish species consumed are also not subject to the state environmental monitoring [9]. The Stockholm Convention has pledged member states to encourage and implement at both national and international levels for appropriate research, monitoring and cooperation [19]. The Russian state monitoring system has not yet been able to adapt rapidly to international obligations. As a result, there is a concern for the health of fish, wildlife and humans who consume local food [10,20]. Recently, a long-term study was initiated to monitor changes in the amounts of POPs and PIPs in the diet of pan-Russian Arctic indigenous populations by establishing an Arctic biomonitoring laboratory in the Northern (Arctic) Federal University since 2017 [21]. This part of the study presents the concentrations of priority POPs in five fish species: pink salmon, Arctic char, navaga, northern pike and humpback whitefish, which are among the most commonly consumed species by indigenous peoples of coastal villages of Nenets Autonomous Okrug (NAO).

2. Materials and Methods

2.1. Sampling Strategy

Indiga is one of the largest settlements of the Nenets Autonomous Okrug, Russia, located on the Barents Sea coast [22]. The fish species were selected on the basis of a nutritional survey among the population of the village. According to the questionnaire, which was published earlier [23], the fish consumed by indigenous peoples in the area mainly belong to the families Salmonidae (62%) and Gadidae (15%). Salmon fish (pink salmon, Arctic char and humpback whitefish) and a representative cod (navaga) were bought from local fishermen in 2017–2018. Northern pike from the Pechora River (Barents Sea basin) was chosen as a freshwater predator species. The number of fish collected ranged

from 8 to 12 samples depending on the fish species. Transportation, storage, age determination and preparation of samples for analysis was performed in our previous work [22].

2.2. Reagents and Materials

The choice of congeners is justified by their presence in the Stockholm Convention on Persistent Organic Pollutants. High purity single analytical standards of the following polychlorinated biphenyl (PCB) congeners: #28, 52, 101, 105, 118, 123, 128, 153, 180, 183, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, hexachlorobenzene, cis-nonachlor, trans-nonachlor, cis-chlordane, trans-chlordane, mirex, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, β -heptachloroepoxide, aldrin and heptachlor were chosen.

HPLC-grade acetone, hexane, Florisil (60–100 mesh) and all high-purity analyte standards were obtained from Sigma-Aldrich (Steinheim, Germany). Labeled $^{13}\text{C}_{12}$ PCB#101 used was from Cambridge Isotope Laboratories (USA). Sulfuric acid (98% purity) was purchased from Supelco (Bellefonte, PA, USA). Helium (99.9999% purity) and nitrogen (99.9999% purity) were from NIIKM (Moscow, Russia).

2.3. Determination of POP

Determination of POPs was performed using an Agilent 7890A gas chromatography (GC) system equipped with an Agilent 7000 series MS/MS triple quadrupole system (USA).

Data acquisition and processing were done using the Agilent MassHunter QQQ Quantitative Analysis B.05.00 software. An Agilent ultra inert GC column (HP-5MS UI, 30 m \times 0.25 mm \times 0.25 μm) connected to a Restek Guard column (Rtx-5M) was used throughout for analytes separation.

The portions of the extracts (1 μL) were injected using a multimode injector inlet in splitless mode through an ultra inlet liner with a glass wool frit (Agilent 5190-2293). The injector temperature was 250 $^{\circ}\text{C}$. Helium was used as the carrier and quenching gas, and nitrogen was used as the collision gas. The oven temperature program was as follows: 70 $^{\circ}\text{C}$ for 3 min, up to 150 $^{\circ}\text{C}$ at a rate of 50 $^{\circ}\text{C min}^{-1}$, up to 200 $^{\circ}\text{C}$ at a rate of 3 $^{\circ}\text{C min}^{-1}$ maintained for 1 min, up to 280 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$ maintained for 5 min and finally, up to 310 $^{\circ}\text{C}$ at a rate of 40 $^{\circ}\text{C min}^{-1}$ maintained for 4 min.

The total run time was 38 min with 4 additional minutes for backflushing at 280 $^{\circ}\text{C}$; the pressure was maintained at 70 psi. Constant pressure (18 psi) mode was used. The purge flow to the split vent was 30 mL min^{-1} at 0.75 min. The system was operating in electron-ionization (EI) mode (70 eV). The transfer line temperature was kept at 270 $^{\circ}\text{C}$. The ion source and quadrupole analyzer temperatures were fixed at 230 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$, respectively. The collision gas flow was 1.5 mL min^{-1} and the quenching gas flow was 2.35 mL min^{-1} .

2.4. Optimization of Gas Chromatography and Mass Spectrometry Parameters

For optimization of the MS parameters, all analytes were monitored in full scan mode in the 50–800 m/z range to select the precursor and product ions. The collision energy (CE) was optimized for each transition in a multiple reaction monitoring (MRM) experiment. The most intense transitions were selected as the quantifier transitions, and the second most intense transitions were selected as the qualifier transitions. A 14 time segment method was created to obtain an adequate sensitivity and signal to noise (S/N) ratio. The solvent delay was 9 min.

2.5. Sample Preparation and Clean Up

A 1-gram portion of freeze-dried fish muscle was extracted using 20 mL of a hexane-acetone mixture (1:1 v/v) in a 250 mL conical flask. The flasks were then shaken for 8 h in an IKA KS 260 basic automatic laboratory shaker (IKA-Werke GmbH & Co. KG., Staufen, Germany).

After extraction, the flasks content were transferred to 50 mL polypropylene tubes (PP) (Sarstedt AG & Co. KG, Nümbrecht, Germany) and centrifuged at room temperature for 5 min at 4000 rpm. The resulting supernatants were quantitatively transferred to 200 mL evaporation cups. The tubes

were rinsed with a 20 mL portion of hexane and centrifuged again at room temperature for 5 min at 4000 rpm. This procedure was repeated twice.

The contents of the cups were evaporated at 36 °C to a volume of 0.5–1.0 mL in a stream of nitrogen. The residues after evaporation were transferred to 15 mL polypropylene centrifuge tubes. The evaporation cups were rinsed twice with 7 mL of hexane, and the hexane portions were combined with the residues followed by addition of 1 mL of concentrated sulfuric acid. The tubes were shaken and centrifuged at room temperature for 3 min at 4000 rpm.

After centrifugation, the supernatants were purified on glass columns (10 mm Ø). These columns were filled with Florisil and silica gel. The filled columns were rinsed by gravity with 20 mL of hexane. The wash fraction was discarded.

The persistent organic pollutant residues were washed off, passing through a column of 20 mL of a 6% solution of diethyl ether in hexane. The resulting eluate was evaporated at a temperature of 36 °C in a stream of nitrogen until dry. The dry residue was dissolved in 100 µL of acetone and transferred with a pipette dispenser to a 200 µL micro vial for GC analysis (Agilent, Santa Clara, CA, USA). A measure of 1 µL of internal standard (1 mg/L) was then added.

2.6. Quality Control and Validation

Daily preparation of blank samples and calibration were used. Calibration curves consist of 6 points at 0, 5, 10, 20, 50 and 100 ng/g. Linear regression coefficient values (R^2) ≥ 0.99 . The lowest calibration levels for the majority of analytes were 2–6 ng/g. The validation procedure involved analysis of the fish samples in which one portion was a matrix blank and the other was 20 ppb spiked, yielding 5 replicates; the relative standard deviation (RSD) $\leq 20\%$ and the coefficient of variability (CV) $\leq 33\%$. The spiking procedure for recovery studies was used; to determine the quality of the methodology, a recovery study was performed using standard addition methods. A prior analysis of the samples was performed to detect the target compound. The limits of quantification (LOQs) were calculated by the three methods described elsewhere [24]. The highest value was selected as the LOQ. Certificated reference material (CRM) and 20 ppb spike samples were used for quality assurance and control procedures. The average recovery was: PCB#28 (107%), 52 (108%), 101 (108%), 105 (122%), 118 + 123 (115%), 128 (124%), 138 (116%), 153 (117%), 180 (127%), 183 (109%), HCB (79%), p,p'-DDE (144%), o,p'-DDD (130%), p,p'-DDD (101%), o,p'-DDE (140%), heptachlor (98%), cis-nonachlor (100%), trans-nonachlor (101%), cis-chlordane (122%), trans-chlordane (125%), mirex (60%), Σ tetrachlorobenzene (75%), β -heptachloroepoxide (105%) and aldrin (115%). Labeled $^{13}\text{C}_{12}$ PCB#101 was used as internal standard.

2.7. Lipid Determination

The fat content in the fish muscle was determined by measuring the initial and final mass of the extract. The recommended weight of the sample was ground and extracted into 40 mL of hexane for 40 min in a conical flask. The extract obtained was filtered through a folding filter into a pear-shaped flask, which was previously dried and weighed on an analytical balance. After that, this operation was repeated. The second liquid portion obtained was filtered through the same filter and added to the first portion in the pear-shaped flask. The combined filtrate was evaporated at 67–68 °C, and then the flask was dried in an oven to a constant weight, cooled and weighed on an analytical balance. The weight of the fat sample was defined as the weight of the empty flask minus the weight of the flask with the resulting fat [25].

2.8. Statistical Analysis

For calculations, the software package IBM SPSS Statistics, version 23.0 (IBM Corp., Armonk, New York, NY, USA) was used. The distribution of variables was evaluated visually, and asymmetry was also calculated. The use of parametric analysis (normal data distribution) was not performed, and attempts to normalize the data were futile. To determine the relationships between substances, a

correlation analysis was performed using the Spearman criterion (R) (a nonparametric analog of the correlation analysis).

A two-sided p -value < 0.05 was considered statistically significant. Correlation analysis was used to assess differences between several groups at the same time in order to assess which groups were different from each other and how.

3. Results and Discussion

The lipid content of the fish muscle is highest in the marine species pink salmon and Arctic char with arithmetic mean values of 2.93 and 1.35 wet weight %, respectively.

The weight, age and lipid content of five fish species are presented in Table 1.

Table 1. Arithmetic mean (AM) of weight, age and lipid in fish species.

Fish Species	n	Weight (kg)		Age (Year)		Lipid (%)	
		AM	Min–Max	AM	Min–Max	AM	Min–Max
Arctic char (<i>Salvelinus alpinus</i>)	10	0.73	0.47–1.05	4.5	3.0–6.5	1.37	0.16–3.30
Pink salmon (<i>Oncorhynchus gorbuscha</i>)	12	1.07	0.80–1.64	1+ *	1–2	2.93	2.15–4.73
Navaga (<i>Eleginus nawaga</i>)	10	0.22	0.13–0.38	4.5	3.0–6.5	0.51	0.27–1.03
Humpback whitefish (<i>Coregonus pidschian</i>)	11	0.44	0.38–0.57	7.0	5.0–10.0	0.17	0.02–0.46
Northern pike (<i>Esox lucius</i>)	8	3.45	1.07–6.53	5.0	1.5–8.5	0.10	0.02–0.54

* Age of all fish.

The following POPs were detected in fish: PCB#28, PCB#52, PCB#101, PCB#105, PCB#118, PCB#123, PCB#153, PCB#128, p,p' -DDE, o,p' -DDE, p,p' -DDD, o,p' -DDD, hexachlorobenzene (HCB), cis-nonachlor, trans-nonachlor, cis-chlordane, trans-chlordane, mirex, 1,2,3,5-tetrachlorobenzene and 1,2,4,5-tetrachlorobenzene. Other compounds such as PCB #180, 183, β -heptachloroepoxide, aldrin, and heptachlor were below LOQ.

3.1. PCB Congeners

The POPs with the highest concentrations in the analyzed fish were PCB congeners and dichlorodiphenyltrichloroethane (DDT) breakdown products. This supports the finding by Bonito et al. [26] that the most common organochlorine pollutants in fish are PCBs.

In our study, Arctic char and pink salmon had the highest \sum PCB₈ concentrations of the 5 species studied with mean concentrations of 1.58 and 1.54 ng/g wet weight (ww), respectively. The lowest mean concentrations were present in northern pike muscle (\sum PCB₈ of 0.32 ng/g (ww)) (Table 2).

PCB#153 was the dominant PCB congener, which was found in all fish species except northern pike, and the highest mean concentration was found in navaga (0.68 ng/g, ww) (Figure 1). When exploring other territories such as Western Europe, Asia and Africa, the presence of PCB#153 as the main congener in fish has also been confirmed [15,16,27,28]. Navaga, which contains little fat in muscles, is a marine cod species, as are freshwater northern pike and humpback whitefish.

Table 2. Concentrations of persistent organic pollutants in fish muscle from Nenets Autonomous Okrug.

Analytes, ng/g (ww)	Limit of Quantification (LOQ)	Limit of Detection (LOD)	Arctic Char (N = 10)		Pink Salmon (N = 12)		Navaga (N = 10)		Humpback Whitefish (N = 11)		Northern Pike (N = 8)	
			AM	Min–Max	AM	Min–Max	AM	Min–Max	AM	Min–Max	AM	Min–Max
∑PCB ₈	0.03	0.008	1.58	0.56–2.44	1.54	0.41–2.89	1.24	0.46–2.59	0.72	0.34–1.45	0.32	0.09–0.50
DL-PCB *			0.19	0.11–0.25	0.21	0.02–0.38	0.13	0–0.21	-	-	-	-
NDL-PCB **			1.39	0.45–2.20	1.20	0.40–1.97	1.10	0.38–2.38	0.72	0.34–1.45	0.43	0–0.5
∑DDT	0.03	0.009	0.66	0.33–1.11	2.04	0.50–3.95	0.55	0.18–0.88	0.63	0.27–1.25	0.08	0.03–0.15
HCB	0.03	0.010	0.31	0.04–0.85	0.40	0.12–0.63	0.39	0.14–0.70	0.28	0.02–0.95	0.13	0.03–0.29
∑Tetrachlorobenzene	0.004	0.001	0.02	0.01–0.04	0.02	0.01–0.03	0.02	0.01–0.06	0.17	0.09–0.35		<LOD
Mirex	0.01	0.003	0.05	0.04–0.08	0.13	0.10–0.16	0.04	0.01–0.06	0.06	0.01–0.33		<LOD
cis-Nonachlor	0.12	0.040	0.07	0.06–0.10	0.17	0.06–0.30	0.08	0.06–0.20		<LOD		<LOD
trans-Nonachlor	0.08	0.027	0.13	0.04–0.31	0.40	0.12–0.71	0.07	0.03–0.12		<LOD		<LOD
trans-Chlordane	0.04	0.013	0.03	0.02–0.06	0.10	0.04–0.16	0.03	0.02–0.04		<LOD		<LOD
cis-Chlordane(ng/g)	0.04	0.013	0.05	0.02–0.09	0.17	0.06–0.29	0.04	0.02–0.09		<LOD		<LOD
β-Heptachlor epoxide	0.03	0.010		<LOD		<LOD		<LOD		<LOD		<LOD
Aldrin	0.04	0.013		<LOD		<LOD		<LOD		<LOD		<LOD
Heptachlor	0.05	0.016		<LOD		<LOD		<LOD		<LOD		<LOD

* DL-PCB (105, 118, 123). ** NDL-PCB (28, 52, 101, 128, 153).

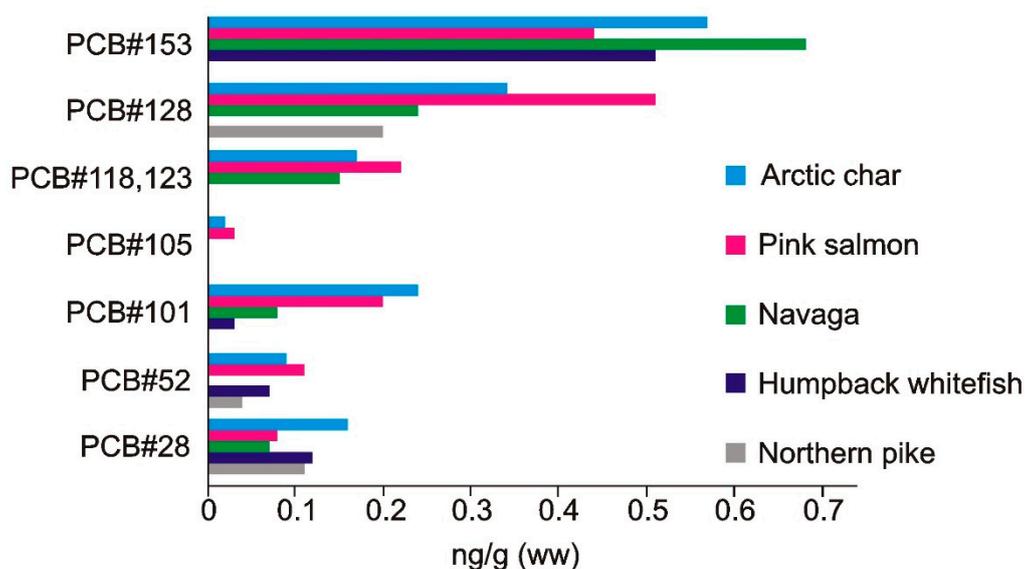


Figure 1. Average medium concentration of PCBs in fish muscle.

As shown in Figure 1, another prevailing PCB congener was PCB#128. The highest mean concentration was present in pink salmon (0.51 ng/g (ww)). In humpback whitefish, this congener was below the detection limit.

Comparing the data in the present study (Table 2) with those reported by Muir et al. (2003) [17], they show that the concentration of Σ PCB congeners in the same or closely related species of fish from NAO was generally lower than in fish caught in the White Sea in the 2000s. Thus, in the present study, the Σ PCB showed that the concentrations of these compounds were 16 times lower in navaga caught downstream of the Indiga River. In addition, the mean concentration of Σ PCB congeners in the northern pike in the present study was approximately 4 times lower than in the pike from the Kola Peninsula, and 7 times lower than in the pike from Chukotka Peninsula. For whitefish, the mean concentration of Σ PCB congeners was 3 to 4 times lower than in AMAP 2004 [29]. The results of the present study show that the Σ PCB concentration in fish has decreased over the past 18 years in the North. This indicates that PCB reduction is a worldwide trend [26].

PCBs can be divided into dioxin-like PCBs (DL-PCBs), whose chemical structure and steric configuration are similar to dioxins, and non-dioxin-like (NDL-PCBs). In the present study, the DL-PCBs were PCB#105, PCB#118 and PCB#123. Despite the fact that the value of Σ PCBs in Arctic char and pink salmon was approximately similar, the Σ DL-PCB in pink salmon (0.25 ng/g (ww)) was higher than that in Arctic char (0.19 ng/g (ww)). In humpback whitefish and northern pike, DL-PCBs were not detected. In navaga, this value was (0.15 ng/g (ww)), but the ratio of Σ DL-PCB to the total PCB content was the same as in Arctic char and amounted to 12%. Additionally, fish with low amounts of NDL-PCBs contain less DL-PCB.

3.2. DDT Breakdown Products

DDT breakdown products were also found in the fish muscles. The Σ DDT means the sum of the following analytes: p,p'-DDE, p,p'-DDD, o,p-DDE and o,p-DDD. Pink salmon had the highest mean concentration Σ DDT (2.04 ng/g (ww)). The lowest mean concentration was present in northern pike (0.08 ng/g (ww)) (Table 2).

In the present study, p,p'-DDE was the main DDT breakdown product residue, and this same result has also been observed in other studies [17,30] (Figure 2).

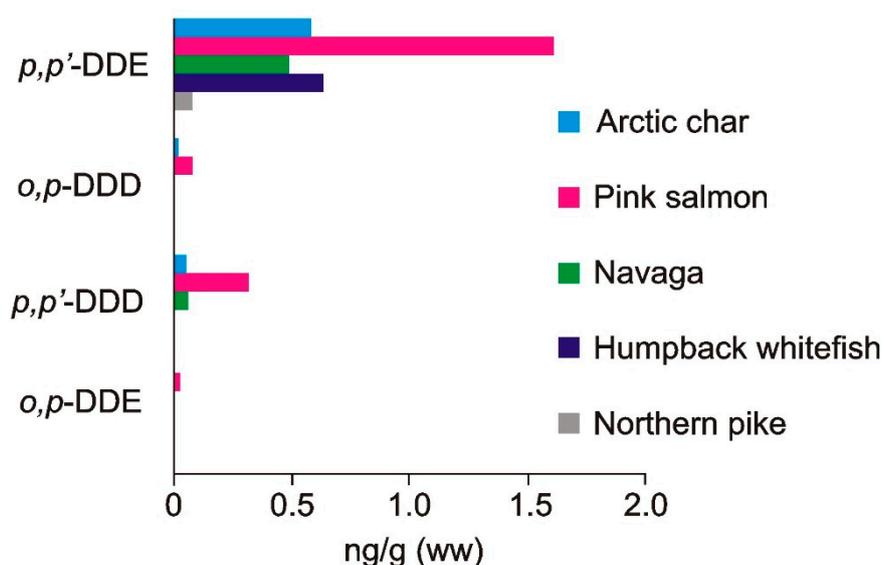


Figure 2. Average medium concentration of DDT breakdown product in fish muscle.

In Arctic char, pink salmon, navaga, humpback whitefish and northern pike, the concentration of p,p'-DDE was 0.58, 1.61, 0.49, 0.63 and 0.08 ng/g (ww), respectively. DDD was the next major DDT residue contaminant in fish, especially in pink salmon. The Σ DDT concentration in navaga caught in NAO was 28 times lower than that found in navaga caught in the White Sea [17]. Σ DDT congeners in whitefish from NAO were 3 to 4 times lower than in whitefish presented in AMAP 2004 [29]; thus, the concentration in whitefish from the Pechora basin (1.6 ng/g (ww)) compared with present results (0.63 ng/g (ww)). However, the concentration of p,p'-DDE was nearly at the same level of 0.63 ng/g (ww) in our study compared with 0.43 to 1.1 ng/g (ww) in AMAP 2004 [29]. The highest mean concentration was found in pink salmon (1.61 ng/g (ww)), which was slightly higher than the 0.53 ng/g (ww) presented by Tsygankov et al. [30].

In four fish species, the total amount of PCBs was higher than Σ DDT. In Arctic char, the concentration of Σ PCB was 2.4 times higher than that of Σ DDT; in navaga, humpback whitefish and northern pike, it was 2.25, 1.14 and 4.0 times higher, respectively. The exception was pink salmon, where the total amount of PCBs was 0.75 times lower than Σ DDT. In addition, the average age of pink salmon in the present study was 1+ years, and from this we can conclude that the rate of DDT accumulation is greater than that of the accumulation of PCB.

3.3. Other POPs

Along with PCBs and DDTs, other POP were found in fish samples such as HCB, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor and mirex. HCB was measured in all fish species ranging from 0.13 ng/g (ww) in northern pike to 0.40 ng/g (ww) in pink salmon (Table 2). The concentration of HCB was only 1.6 times lower than in navaga from the White Sea [26]. However, the concentration was slightly higher or approximately at the same level compared with AMAP 2004 [29]. This is likely due to a lower biodegradation rate for HCB than PCBs.

Most of the other analytes in northern pike and humpback whitefish were less than the detection limit. β -Heptachlor epoxide, aldrin and heptachlor were less than the detection limit for all fish species. Muir et al. [17] present data on the content of heptachlor in fish samples (0.05–0.44 ng/g (ww)).

Chlordane-related compounds (cis-chlordane, trans-chlordane) and nonachlor-related compounds (cis-nonachlor, trans-nonachlor) were present at low mean concentrations in all species and were lower than those presented by Muir et al. [17]. The highest sum concentration was observed in pink salmon with 0.84 ng/g (ww), whereas in Arctic char and navaga, it was 0.28 and 0.22 ng/g (ww), respectively, and while in humpback whitefish and northern pike, it was below the limit of detection (LOD).

The amounts of mirex (0.04–0.13 ng/g (ww)) were practically at the same level as AMAP from 2004 [29] (<0.05–0.13 ng/g (ww)), which indicates its resistance to biodegrade. Compared with the landlocked char from lakes in the Canadian High Arctic reported by Ana Cabrerizo et al. (2018) [31], the concentration of POP in the present study was significantly lower. Visually, the contents of the main analytes and POP groups are shown in Figure 3.

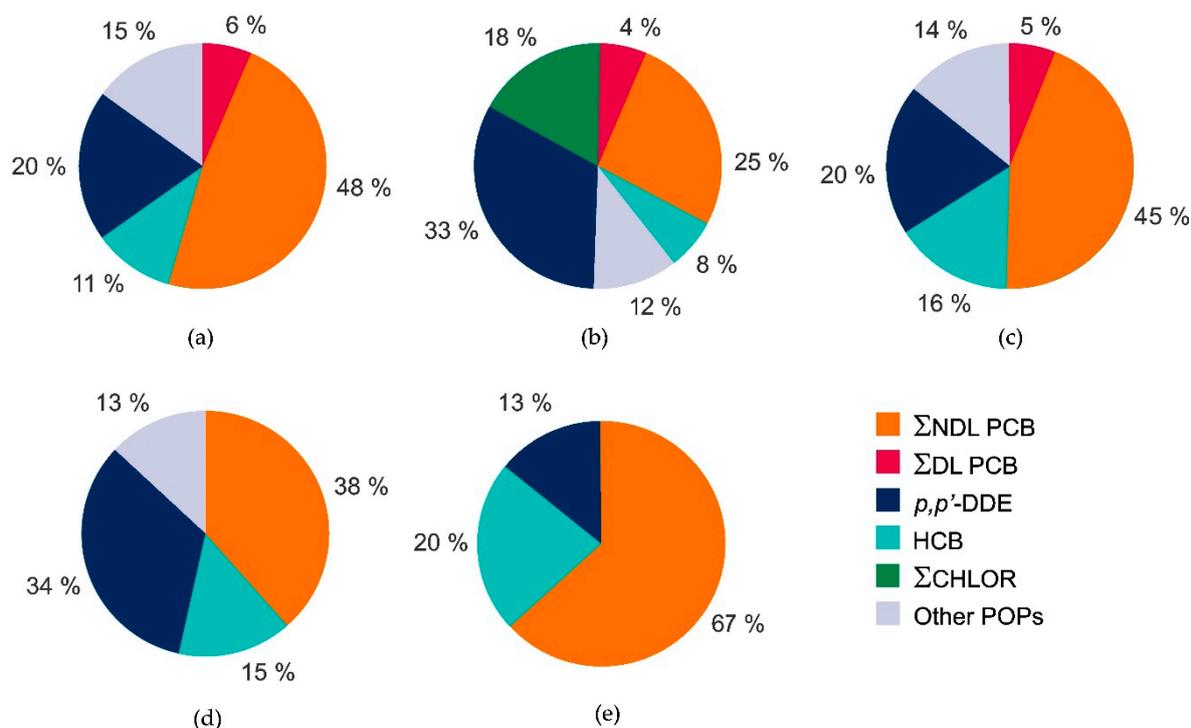


Figure 3. The ratio of DL-PCB and NDL-PCB in various fish species: (a) Arctic char, (b) pink salmon, (c) navaga, (d) humpback whitefish and (e) northern pike.

Figure 3 shows that the main compounds in fish are p,p'-DDE and Σ NDL-PCB. In all fish species, the predominant POP were NDL-PCB, except pink salmon, where p,p'-DDE was the predominant compound. The group "others" includes nonachlors, chlordanes, mirex and the remaining DDT breakdown products. An exception was pink salmon, where chlordanes and nonachlors were allocated to a separate group because their number occupies a significant percentage of the remaining POP.

3.4. Correlation Analysis

In all studied fish with a high fat content (especially pink salmon), the content of POP increased (R values ranged from 0.445 to 0.866; $p < 0.01$ to 0.05) (Table 3). This dependence is especially pronounced for Σ DDT (R = 0.724), trans-nonachlor (R = 0.733), trans-chlordane (R = 0.866) and cis-chlordane (R = 0.800). The correlation between POP and lipid content is presented in Figure 4.

Table 3. Univariate associations (Spearman r and p-values (R)) between elements in all fish (n $\frac{1}{4}$ 51).

	PCB 52	PCB 101	PCB 105	PCB 118,123	PCB 128	PCB 153	∑PCB	∑DDT	HCB	cis- Nonachlor	trans- Nonachlor	trans- Chlordane	cis- Chlordane	Mirex	∑Tetrachloro- Benzene	Lipid	Weight	Age
PCB#28	0.461 **	0.424 **	0.330	0.246	0.384 *	0.406 **	0.400 **	0.215	0.338 *	0.056	0.315	0.231	0.202	-0.156	-0.090	0.054	0.135	0.162
PCB#52		0.637 **	0.654 **	0.664 **	0.726 **	0.338 *	0.644 **	0.695 **	0.463 **	0.577 **	0.831 **	0.784 **	0.738 **	0.332 *	-0.110	0.550 **	0.439 **	-0.174
PCB#101			0.459 *	0.673 **	0.680 **	0.486 **	0.840 **	0.536 **	0.392 **	0.335	0.558 **	0.510 **	0.423 *	0.490 **	-0.499 **	0.658 **	0.529 **	-0.379 *
PCB#105				0.589 **	0.656 **	0.522 *	0.646 **	0.542 **	0.357	0.521 *	0.541 **	0.509 *	0.523 *	0.326	0.138	0.445 *	0.449 *	-0.014
PCB#118,123					0.791 **	0.706 **	0.837 **	0.836 **	0.727 **	0.650 **	0.658 **	0.673 **	0.608 **	0.524 **	0.348	0.590 **	0.403 *	-0.191
PCB#128						0.486 **	0.825 **	0.725 **	0.388 *	0.689 **	0.816 **	0.695 **	0.694 **	0.358 *	-0.188	0.520 **	0.244	-0.286
PCB#153							0.763 **	0.413 **	0.537 **	0.232	0.124	0.098	0.058	0.063	0.017	0.107	-0.102	0.188
∑PCB								0.779 **	0.663 **	0.527 **	0.590 **	0.508 **	0.471 **	0.328 *	-0.379 *	0.638 **	-0.072	-0.280 *
∑DDT									0.596 **	0.821 **	0.914 **	0.901 **	0.864 **	0.603 **	-0.135	0.724 **	0.025	-0.360 **
HCB										0.461 **	0.274	0.434 *	0.390 *	0.171	0.073	0.543 **	-0.127	-0.188
cis-Nonachlor											0.773 **	0.842 **	0.871 **	0.667 **	0.066	0.654 **	0.605 **	-0.441 *
trans-Nonachlor												0.901 **	0.883 **	0.695 **	-0.146	0.733 **	0.749 **	-0.603 **
trans-Chlordane													0.941 **	0.808 **	0.038	0.866 **	0.799 **	-0.508 **
cis-Chlordane														0.749 **	-0.036	0.800 **	0.746 **	-0.484 **
Mirex															-0.315 *	0.708 **	0.615 **	-0.651 **
∑Tetrachloro-benzene																-0.499 **	-0.269	0.611 **
Lipid																	0.107	-0.616 **
Weight																		-0.212

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

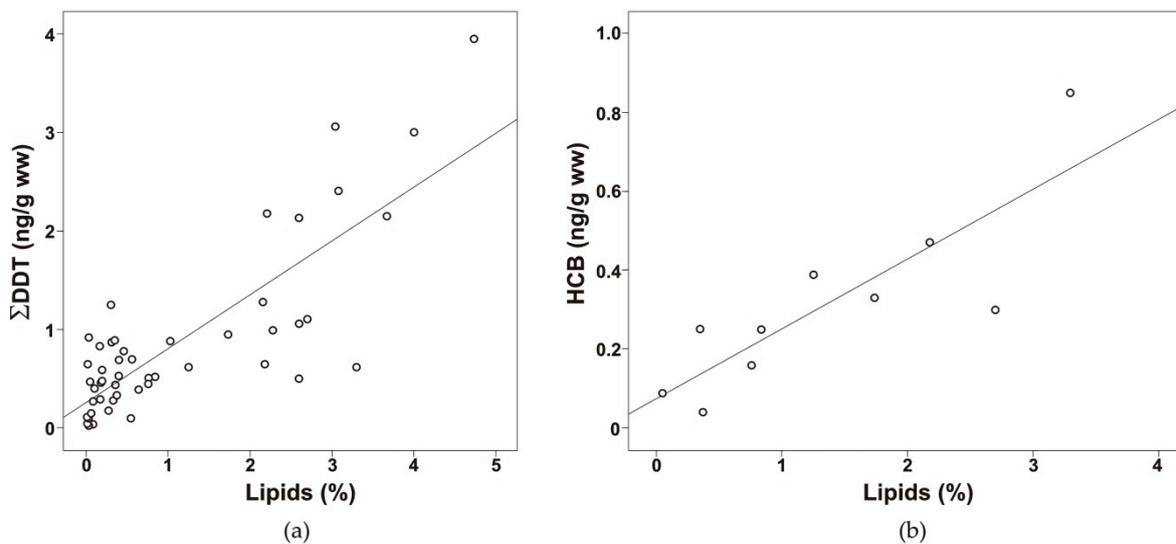


Figure 4. Correlation between POP and lipid content, (a) between Σ DDT and lipid content in all fish samples and (b) between HCB and lipid content in Arctic char samples.

Figure 4 shows a strong positive correlation between Σ DDT and lipid content in all fish. Some fish species have individual correlations between analyte and lipid content, such as the correlation between HCB and lipid content in Arctic char.

However, in some samples, the weight of the sample affects the content of POP, and Spearman's correlation coefficient varies from 0.403 to 0.799. In navaga weighing between 0.125–0.380 kg, cis-chlordane accumulates to a greater extent (Figure 5), indicating accumulation, and this is partly because old (large) fish have been exposed to cis-chlordane for a longer time than young (small) fish.

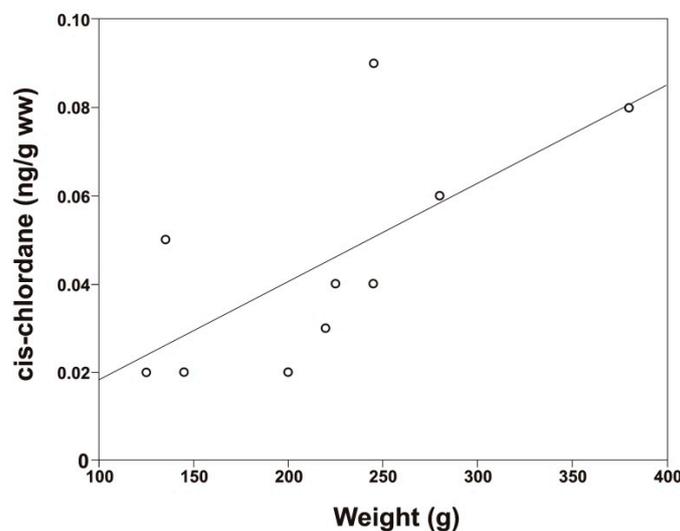


Figure 5. Correlation between cis-chlordane and weight in navaga.

However, in most fish samples, no statistically significant relationships between POP concentration and fish weight were found; the same results were observed by Cabrerizo et al. [31].

In addition, the current study revealed the relationship between several congeners (Table 3.) A strong positive relationship between Σ PCB and Σ DDT was observed by comparing all types of analyzed fish ($R = 0.779$). A strong positive correlation was observed between Σ DDT and cis-nonachlor ($R = 0.821$), trans-nonachlor ($R = 0.914$), trans-chlordane ($R = 0.901$) and cis-chlordane ($R = 0.864$). Additionally, a strong positive relationship was observed between PCB#52 and PCB#128 ($R = 0.726$).

and between PCB#128 and PCB#118,123 ($R = 0.791$). A strong positive correlation was observed between PCB#153 and p,p' -DDE (Figure 6). The same correlation was observed by Storelli et al. [32].

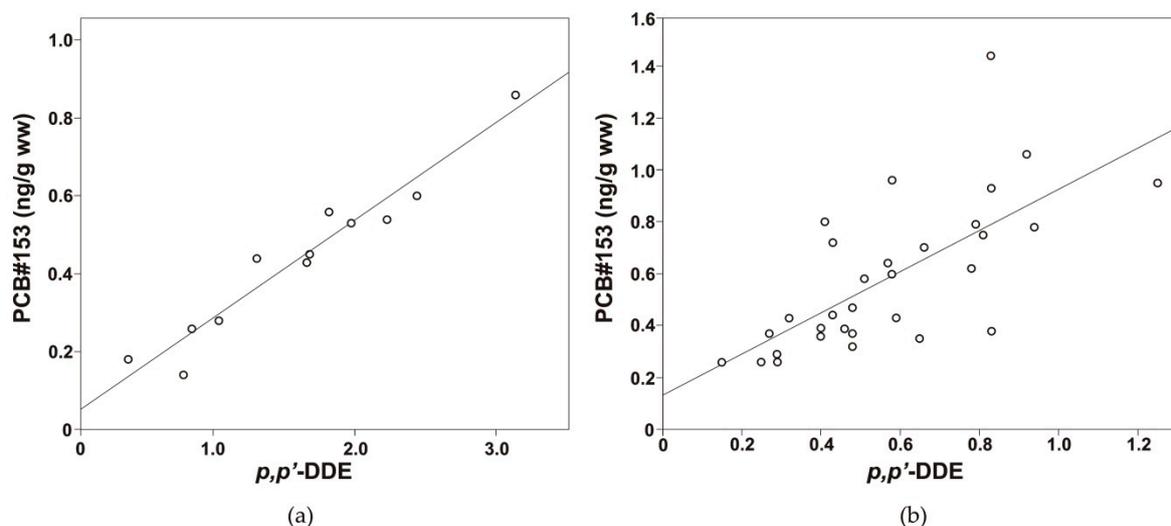


Figure 6. Correlation between PCB#153 and p,p' -DDE in (a) pink salmon and (b) other fish species.

Due to the higher ratio of \sum DDT to \sum PCB, the correlation between PCB#153 and p,p' -DDE for pink salmon does not fit the general correlation between PCB#153 and p,p' -DDE for other fish. Therefore, it is presented separately.

Such a high ratio suggests that these POPs can come from similar sources and reflect old pollution, which may be background pollution in this area. Thus, the main factor in the accumulation of POP is lipid content. There was also a link of major POPs with each other.

4. Conclusions

The major POPs in fish from the NAO were DDT-related compounds and PCBs. The amounts of \sum PCB₈ and \sum DDT were relatively low in all fish species and did not exceed 10 ng/g wet wt. A relationship between fat content in the fish and POP concentration was found, and fatty fish (pink salmon, Arctic char) from the Barents Sea basin contain 2 or more times higher concentrations of POP compared with lower fat fish (northern pike, humpback whitefish). A strong positive correlation was observed between \sum PCB and \sum DDT, \sum DDT and lipid contents and \sum DDT and chlordane and nonachlor. Despite the large number of fish in the diet of indigenous peoples from NAO, no significant risks were identified. Most legacy POP and OCPs tend to decrease, which can be explained by the past national and regional bans and the restriction on their use and emission. The aim of further research will be an expansion of the list of analytes and species including human blood.

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