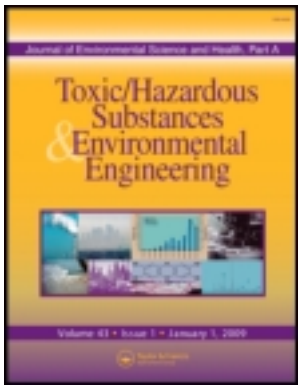

Journal of Environmental Science and Health, Part A
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lesa20

Hydrocarbon products and their derivatives in fish of the Pechora River, North-Eastern European Russia

Anatoly A. Lukin [a b], Guttorm N. Christiansen [c], Geir A. Dahl-Hansen [c], Julia N. Sharova [a d] & Lidia A. Belicheva [d]

[a] Akvaplan-niva Barents, Murmansk, Russia

[b] Institute of North Industrial Ecology Problems, Apatity, Russia

[c] Akvaplan-niva, Tromsø, Norway

[d] Northern Water Problems Institute, Russian Academy of Science, Petrozavodsk, Russia

Available online: 15 Jul 2011

To cite this article: Anatoly A. Lukin, Guttorm N. Christiansen, Geir A. Dahl-Hansen, Julia N. Sharova & Lidia A. Belicheva (2011): Hydrocarbon products and their derivatives in fish of the Pechora River, North-Eastern European Russia, Journal of Environmental Science and Health, Part A, 46:10, 1035-1041

To link to this article: http://dx.doi.org/10.1080/10934529.2011.590379

Journal of Environmental Science and Health, Part A (2011) **46**, 1035–1041

ISSN: 1093-4529 (Print); 1532-4117 (Online)
DOI: 10.1080/10934529.2011.590379

Taylor & Francis
Taylor & Francis Group

Hydrocarbon products and their derivatives in fish of the Pechora River, North-Eastern European Russia

ANATOLY A. LUKIN[1,2], GUTTORM N. CHRISTIANSEN[3], GEIR A. DAHL-HANSEN[3], JULIA N. SHAROVA[1,4] and LIDIA A. BELICHEVA[4]

[1]*Akvaplan-niva Barents, Murmansk, Russia*
[2]*Institute of North Industrial Ecology Problems, Apatity, Russia*
[3]*Akvaplan-niva, Tromsø, Norway*
[4]*Northern Water Problems Institute, Russian Academy of Science, Petrozavodsk, Russia*

Analysis of one of the major surface oil spill consequences, which took place in 1994 on the territory of the Pechora River (Russia) catchment area, was carried out. Data on hydrocarbon products and their derivatives concentrations in muscle and liver tissues of several fish species living in the Pechora's Delta and the river tributaries were obtained. Comparative analysis of OCCs, PCBs and PAHs concentrations in 1997 and 2008 showed that levels of all examined pollutants in fish tissues are very low. At the same time, in 2008 OCCs and PCBs concentrations in fish were lower compared to 1997, except for PAHs concentrations in Pechora Delta whitefish, which demonstrate the opposite tendency in relation to two compounds for the last 11 years.

Keywords: Organochlorine compounds, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, fish, concentration, liver, muscles.

Introduction

The Pechora River basin is one of the largest basins in Northwest Russia, with a catchment area of 327,000 km^2. The Timano-Pechorskaya oil-and-gas province located there determines increased anthropogenic load associated with oil and gas production and transportation in the region. The Pechora River mainstream and tributaries are crossed by numerous oil pipelines, where emergencies are frequent enough. Therefore, oil pollution is one of the most pressing problems for the Pechora ecosystem. Our investigations in the Pechora River catchment area, carried out at the end of the 1990s, revealed that anthropogenic load have multiplied since 1960s–70s due to the new territory exploration.[1]

Taking into account vulnerability of northern nature, it is necessary to have clear view of the processes that take place in water and land ecosystems under anthropogenic impact. So the search of indicators for the assessment of the anthropogenic impact level is pressing problem. Fish that inhabit Sub-Arctic fresh water bodies are highly sensitive to water quality. Environmental changes due to the human activity induce rapid response in fish organism and that fact enable us to use fish as test-organisms, which reflect the state of environment. Comparative analysis of organochlorine compounds (OCC), polychlorinated biphenyls (PCB), and polycyclic aromatic hydrocarbons (PAH) accumulation and distribution in liver and muscle tissues of fish can be used as a measure of persistent organic pollutants (POP) load on the Pechora region water ecosystem.

Address correspondence to Julia Sharova, Northern Water Problems Institute, Russian Academy of Science, Petrozavodsk, Russia; E-mail: jul.sharova@yandex.ru, jsharova@inbox.ru
Received December 7, 2010.

Materials and methods

Experimental design, sampling and sample preparation

In the summer and autumn of 2008, field work in the Pechora catchment area was carried out. Samples were collected from the Pechora's Delta (Korovinskaya Bay), Pechora's largest tributary – river Usa, and Usa's tributary – river Kolva (Fig. 1).

Fish was caught by stake gill nets (length – 30–50 m, height – 1.7–2 m, mesh size – 40–55 mm), drift nets (length – 150 m, mesh size – 40 mm) and seine. The ide (*Leuciscus idus*), vendace (*Coregonus albula*), and whitefish (*Coregonus lavuretus*) were used at present study as they are commonly found fish species in the examined area. Accumulation and distribution of a number of OCCs, PCBs, and PAHs were analyzed. The liver and muscle of 10 fish of each species were sampled for analysis.

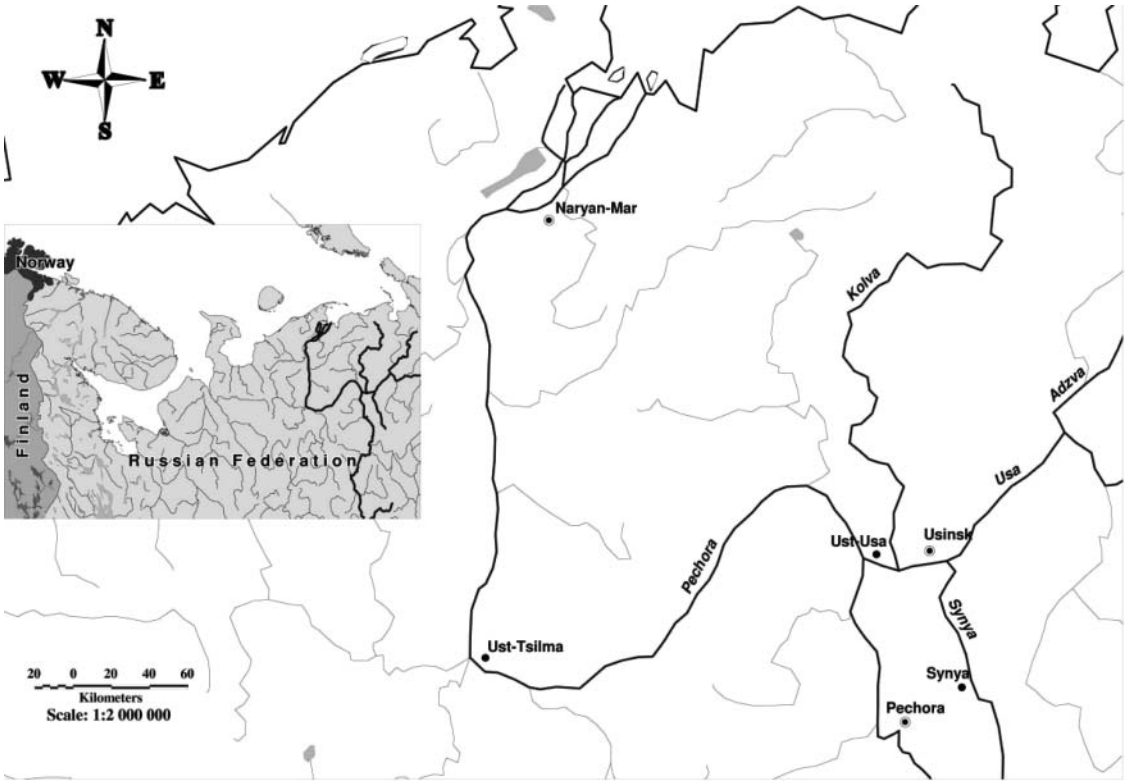

Fig. 1. A map of the Pechora River Basin (East part of Sub-Arctic Russia).

Analytical procedure

OCCs, PCBs and PAHs levels were determined in the analytical laboratory of the Institute for Problems of Environmental Monitoring (IPEM), Research and Production Association 'Typhoon' center (Obninsk, Russia). Liver and muscle tissues of specimens were analyzed in groups. Each group includes 8–10 samples, control sample with known concentration of assessed compounds, and procedural blank. For POPs extraction control, surrogate standards were applied in each sample: for OCCs analysis, octachlornaphthalene and d–HCH were added; for PCB congeners analysis, PCB#30 and PCB#112 were added; for PAHs analysis, naphthalene-d48, acenaphthylene-d10, phenanthrene-d10, chrysene-d12, perylene-d12 were added. For OCCs and PCBs analysis, PCB#166 was used as an internal standard, for PAHs analysis, 1-bromadamantane was used.

Specimens were defrosted under room temperature and homogenized using microgrinder. Weighted specimen was ground with anhydrous sodium sulfate to uniform mass. After surrogate standards were added, specimen was transferred to glass column and undergone hexane: methylene chloride (1:1) mixture extraction. Extract was concentrated on rotor-type evaporator for further chromatographic purification. Purification of extracts from lipid was carried out using glass columns with Teflon valve filled with Bio-Beads SX-3 sorbent (20 g).

Concentrated extract (2 mL) and hexane: methylene chloride (1:1) mixture (50 mL) were transferred in washed column. The fraction was used for lipid detection. After that mixture containing determinate substances (50 mL) was collected in round-bottomed flask and concentrated in rotor-type evaporator to 0.5 mL for further purification.

For PCBs and OCC analysis, concentrated extract was quantitively transferred to column filled with deactivate silica gel (3 g, 3%). Column was eluted with hexane (20 mL) (fraction–I), then with hexane: methylene chloride (1:1) mixture (35 mL) (fraction–II). Both fractions were concentrated using rotor-type evaporator, transferred to micro vials and concentrated under nitrogen flow to 30–50 μL.

Extract purification for PAHs determination was carried out using columns filled with deactivate silica gel (10 g, 3%). Columns were eluted with hexane (25 mL) (fraction I), and hexane: methylene chloride (1:4) mixture (55 mL) after that (fraction II). Second fraction containing PAHs was concentrated using rotor-type evaporator and transferred to micro vials and subsequently concentrated under nitrogen flow to 30–50 μL. Before instrumental analysis appropriate internal standard was added in each specimens.

OCCs and PCBs analysis was carried out using a Hewlett-Packard GC/ECD 5790A gas chromataograph. PAH content was determined using a HP 5972 massspectrometer HP 5972. Possible specimens contamination during the sample preparation and instrumental analysis was assessed by the results of procedural blank sample analysis.

Table 1. Concentrations of different OCCs in fish tissues (ng g^{-1} wet weight).

	1997					*2008*		
	Kolva		*Usa*					
	Whitefish	*Vendace*	*Vendace*	*Ide*	*Whitefish*	*Kolva Ide*	*Usa Whitefish*	*Korovinskaya Bay Whitefish*
HCB	2.70	1.60	3.20	2.40	3.60	0.81	0.58	1.01
	0.84	0.92	2.10	1.45	0.52	0.16	0.04	0.11
α-HCH	1.40	n.d.	1.10	1.35	2.70	0.01	0.03	0.07
	0.71	n.d.	0.34	n.d.	0.64	0.05	n.d.	n.d.
β-HCH	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.02	0.13
	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.02	0.02
γ-HCH	0.95	0.95	0.71	1.12	2.10	0.15	0.01	0.16
	0.42	0.20	0.28	0.73	0.37	0.03	n.d.	0.01
Heptachlor	1.70	1.40	0.85	9.70	0.50	n.d.	0.21	n.d.
	0.67	1.30	0.50	0.71	0.74	n.d.	n.d.	n.d.
trans-Chlordane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
cis-Chlordane	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.01	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
trans-Nonachlor	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	n.d.	0.03
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4 DDE	0.75	0.58	0.25	0.23	1.70	0.10	0.06	0.09
	0.22	0.39	0.31	1.71	0.26	n.d.	n.d.	n.d.
4,4 DDE	2.40	4.10	4.40	9.10	2.80	0.84	0.56	1.26
	0.56	1.90	2.20	0.76	0.69	0.13	0.09	0.245
2,4 DDD	n.d.	0.25	n.d.	n.d.	n.d.	0.02	0.03	0.18
	n.d.	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4,4 DDD	1.05	0. 91	0.90	0.87	0.60	0.21	0.25	0.52
	n.d.	0.85	0.94	n.d.	n.d.	n.d.	0.02	0.045
2,4 DDT	n.d.	n.d.	1.20	0.64	n.d.	0.07	0.08	0.15
	n.d.	n.d.	0.25	n.d.	n.d.	n.d.	n.d.	n.d.
4,4 DDT	0.78	0.69	2.00	1.57	0.49	0.05	0.19	0.28
	0.36	0.42	0.59	n.d.	0.31	n.d.	n.d.	0.03
Mirex	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Aldrin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Epoxide	0.46	0.21	n.d.	2.20	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*Values in numerator are concentration of substances in liver, values in denominator are concentrations of substances in muscles; n.d. means not detected.

Certified standard biological material SRM 2974 was used as a control.

The results of the present study were compared with the results of the investigation that was carried out at the same stations in 1997. In 1997 the analysis were carried out in the international certified analytical laboratory of the "Arctic Monitoring" regional Centre (St. Petersburg).

Results

OCCs concentrations

Seventeen different OCCs were analyzed in the liver and muscle tissues of Pechora fish (whitefish, vendace, ide). The level of examined pollutants was either very low or under detection limit (Table 1). It is quite difficult to detect differences in OCCs accumulation among the studied fish species, as concentrations of studied substances both in coregonids and cyprinids were at about the same level (Table 1).

In 1997 the highest concentration of substances such as hexachlorbenzol was observed in the liver of Kolva whitefish, Usa whitefish and vendace (Table 1). In the liver of Usa ide, the concentration of this pollutant was slightly lower (Table 1). However, in 1997 liver tissue of ide from the Usa river was characterized by the highest concentration of heptachlor (9.7 ng g^{-1} wet weight) and 4,4-DDE (9.10 ng g^{-1} wet weight) (Table 1).

Table 2. Concentrations of several PCB congeners in fish tissues (ng g^{-1} wet weight).

	1997							
	Kolva		*Usa*			*2008*		
	Whitefish	*Vendace*	*Vendace*	*Ide*	*Whitefish*	*Kolva Ide*	*Usa Whitefish*	*Korovinskaya Bay Whitefish*
PCB#52	n.d.	n.d.	n.d.	n.d.	n.d.	0.27	0.22	0.28
	n.d.	n.d.	n.d.	n.d.	n.d.	0.29	0.17	0.17
PCB#101	1.80	0.55	1.10	0.10	0.97	0.73	0.46	0.71
	0.67	n.d.	0.41	0.10	0.57	n.d.	n.d.	0.10
PCB#105	n.d.	n.d.	n.d.	n.d.	n.d.	0.25	0.22	0.24
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB#138	2.00	3.10	1.51	3.70	2.00	0.62	0.68	0.89
	1.55	1.80	0.42	0.31	2.11	n.d.	n.d.	n.d.
PCB#153	3.60	1.10	2.15	1.71	2.80	0.69	0.59	0.77
	0.48	0.35	0.53	0.59	0.75	n.d.	n.d.	0.11
PCB#180	n.d.	n.d.	n.d.	n.d.	n.d.	0.22	0.33	0.35
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.

*Values in numerator are concentration of substances in liver, values in denominator are concentrations of substances in muscles; n.d. means not detected.

The presence of such compounds was revealed in the liver and muscle tissues of all studied fish species in 1997 (Table 1). In 2008, hexachlorbenzol and 4,4-DDE were also present in all examined fish; however the levels of these substances were considerably lower in relation to 1997 (Table 1). In 2008 heptachlor was observed only in the liver of whitefish from the Usa River (Table 1). As for lindane (γ-HCH), in 1997 it was observed in all studied fish species with the highest concentration in the liver tissue of whitefish from the Usa River (2.10 ng g^{-1} wet weight), while 11 years after the concentration of this pollutant decreased in all studied fish (Table 1). Nonetheless, the observed values of the pollutants are very low both in 1997 and 2008.

Research carried out by Norwegian experts in the Pechora lower reach (up- and downstream of Naryan-Mar) in 1997 yielded similar results: thus, OCCs concentration in whitefish, peled, Arctic cisco, inconnu and pike muscles was very low: lindane (γ- HCH) and octachlorostyrene concentrations were undetectable (<0.07 ng g^{-1} wet weight).[2]

PCBs concentrations

PCBs content was at extremely low levels, both in 1997 and 2008 at each of the examined stations, irrespective of the fish species studied (Table 2). From 6 studied congeners, only 3 PCB congeners (PCB#101, PCB#138, PCB#153) were observed in the liver and muscle tissues of fish in 1997 (Table 2). In 2008, all fish showed other liver tissues profiles, in which presence of all studied PCB congeners was revealed. However the concentrations of the PCB#101, PCB#138, PCB#153 congeners decreased compared to 1997 (Table 2). On the whole, chose for comparison PCB congeners have demonstrated stable concentration decrease in the muscle and liver tissues of fish in 2008 compared to 1997 (Table 2).

Looking back at the permissible levels set by the international commission (PCB for intact fish–0.1 μg g^{-1} or 100 ng g^{-1}) one can state that the substances are present in the Pechora fish liver and muscle tissues in concentrations safe for the organism (Table 2).

According to Norwegian researchers,[2] total PCB concentration in the Pechora lower reach (before the delta) was also quite low: the values in whitefish and peled muscles were about 0.3 ng g^{-1} dry weight, while the greatest PCB concentrations were reported for Arctic cisco and inconnu – 1.3 and 0.7 ng g^{-1} dry weight, respectively. According to Scotvold et al,[3] PCBs content in whitefish from northern Norwegian lakes ranges from 0.3 to 0.9 ng g^{-1} dry weight, which is believed to be a background concentrations.

PAHs concentrations

Analysis of 24 individual PAHs indicated their content to be very low in Pechora fish tissues (Table 3). In 1997 the relatively high concentrations of such PAHs as naphthalene and phenanthrene were revealed in the liver of whitefish and vendace from the Kolva and Usa rivers, however, the levels of mentioned substances in the muscle tissue was considerably lower or even under detection limit (Table 3). The level of PAHs which is considered as most toxic (e.g. benzo[*a*]pyrene, perylene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a,h*]anthracene, indeno[1,2,3-*c,d*]pyrene, benzo[*g,h,i*]perylene) was undetectable in the liver and muscle tissues of all studied fish in two studied periods (Table 3). In 2008 analysis of the muscle tissues of ide and whitefish from the Kolva and Usa rivers did not

Table 3. Concentrations of individual PAHs in fish tissues (ng g^{-1} wet weight).

	1997					*2008*		
	Kolva		*Usa*					
	Whitefish	*Vendace*	*Vendace*	*Ide*	*Whitefish*	*Kolva Ide*	*Usa Whitefish*	*Korovinskaya Bay Whitefish*
Naphthalene	32.00	29.00	44.00	n.d.	21.00	3.44	n.d.	37.33
	9.20	n.d.	23.00	n.d.	n.d.	n.d.	n.d.	n.d.
Acenaphthylene	n.d.	n.d.	n.d.	n.d.	n.d.	4.92	n.d.	117.60
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.68
2-Metilnaphthalene	12.00	3.80	8.40	n.d.	3.50	9.74	1.46	116.53
	5.00	n.d.	6.10	n.d.	n.d.	n.d.	n.d.	9.54
1-Metilnaphthalene	4.80	3.10	5.20	n.d.	1,8	n.d.	n.d.	2.71
	1.50	n.d.	3.00	n.d.	n.d.	n.d.	n.d.	n.d.
Fluorene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	12.00	2.10	7.10	6.10	n.d.	n.d.	n.d.	n.d.
Acenaphthene	n.d.	n.d.	n.d.	n.d.	n.d.	1.41	0.32	12. 41
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.05
Phenanthrene	22.00	18.00	17.00	25.00	15.00	5.44	1.22	22.00
	11.00	3.50	5.10	n.d.	4.20	n.d.	n.d.	1.43
Anthracene	1.40	1.40	1.20	1.60	1.80	n.d.	n.d.	0.76
	0.70	0.70	0.80	0.40	0.60	n.d.	n.d.	n.d.
Fluoranthene	n.d.	4.10	1.90	1.80	1.40	0.59	n.d.	2.85
	n.d.	1.70	0.60	n.d.	2.10	n.d.	n.d.	n.d.
Pyrene	4.00	n.d.	4.80	n.d.	n.d.	n.d.	n.d.	2.90
	2.10	2.60	2.00	4.50	n.d.	n.d.	n.d.	n.d.
Benzo[*a*]anthracene	n.d.	n.d.	1.20	0.80	n.d.	0.18	n.d.	0.87
	0.40	2.10	0.90	0.80	1.20	n.d.	n.d.	n.d.
Chrysene	n.d.	n.d.	5.40	n.d.	n.d.	n.d.	n.d.	n.d.
	4.10	2.40	2.40	n.d.	2.60	n.d.	n.d.	n.d.
Benzo[*a*]pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Perylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo[*k*]fluoranthene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo[*a*]pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenz[*a,h*]anthracene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Indeno[1,2,3-*c,d*]pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo[*g,h,i*]perylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*Values in numerator are concentration of substances in liver, values in denominator are concentrations of substances in muscles; n.d. means not detected.

reveal presence of any examined PAHs, while low levels of individual PAHs were observed in fish liver (Table 3).

Similar research carried out on fish from the Rybinskoye storage reservoir revealed PAH concentrations dozens times greater than in the Pechora fish.[4] Studies by Norwegian researchers conducted in 1997 confirmed low PAH content in the muscles of peled, whitefish, inconnu and pike from the Pechora lower reach.[2] Some PAH compounds could not be detected by existing techniques, e.g. benzo[a]pyrene. The greatest total PAH concentrations were recorded in the muscles of Arctic cisco (41.5 μg g^{-1} wet weight) and whitefish (42.5 μg g^{-1} wet weight).[2]

According to Knutzen,[5] total PAH values in fish muscles between 20 and 50 μg/g wet weight, and benzo[a]pyrene between 0.5 and 1 μg g^{-1} wet weight indicate the presence of PAH impact on fish organism. And in our case only two PAH substances (acenaphthylene, 2-methylnaphthalene) are the exclusion, as their content in whitefish from Pechora Delta (Korovinskaya Bay) has multiplied since 1997.[2] It should be noted that little information regarding the acute

or chronic toxicity of acenaphthylene is available, while 2-methylnaphthalene are among the most toxic soluble components of crude oil.[6–9]

Discussion

The level of OCCs in the Pechora fish was evaluated using the scale developed by Rovinskii et al,[10] in which OCCs concentrations were grouped into six levels: I – OCCs not detected, II – below 0.1 μg g^{-1}, III – 0.1–10 μg g^{-1}, IV – 10–100 μg g^{-1}, V – 100–1000 μg g^{-1}, VI – >1000 μg g^{-1}. It is readily seen that all studied OCCs were found in low concentrations corresponding to levels I and II (Table 1).

What are the remarkable facts in the analysis of OCCs content in fish organs and tissues? In 1997 all examined fish were found to contain heptachlor, which must not be present in fish organs and tissues as demanded by OCCs-related health standards.[11] The stringent requirements are apparently prompted by the high accumulation coefficient (ratio between heptachlor concentration in aquatic organisms and its concentration in the water), which may reach 1000 and more.[12] The fact that the substance was found, however, proves that hydrocarbons do enter the Pechora river ecosystem in 1997. In 2008, heptachlor was observed only in the liver of whitefish from the Usa River, and the level was considerably lower compared to 1997.

Analysis of OCCs content also revealed presence of DDT and its breakdown products in liver and muscle tissues of fish from the Pechora River and its tributaries in both studied periods. The data concerning DDT and its derivatives profiles in fish tissues can be explained by the fact that parent compound is not as persistent as its metabolites, so DDT concentrations represent only minor part of the total DDT load in the organism.

PCBs content was at extremely low level both in 1997 and 2008 in the Pechora River and its tributaries irrespective of studied fish species. The fact that PCB congeners are still detected in fish tissues and have shown only little decline in the past 11 years at studied sites, probably indicates that PCBs are still being transported within the river basin through the atmospheric transport, relocation of contaminated sediments. On the other hand, the differences in studied PCB congeners profiles can be related with transboundary pollution.

According to results of the present study such hexachlorobiphenyl congeners as 153 and 138 were the most abundant PCBs detected in fish tissues. These findings support the results of similar studies devoted to the investigation of PCB bioaccumulation profiles in fish tissues.[13,14] It has been shown that congener 153 is especially persistent,[15] and that generally higher chlorinated congeners are slower to be metabolized and eliminated than lower chlorinated congeners.[16]

It is a well-known fact that fish are among the largest potential source for human exposure to PCBs. And in 1993, an advisory group on fishery in Great Lakes elaborated safe level of fish consumption recommendations. The recommendations are based on permissible level of daily PCB intake in human organism that is 3.5 μg PCB per day.[17,18] Relying on the permissible level of PCB intake, 5 groups of possible consumption of PCB polluted fish can be marked:

i. PCB level is less than 0.05 mg kg^{-1} – unlimited consumption
ii. PCB level is from 0.05 to 0.22 mg kg^{-1} – once per week
iii. PCB level is from 0.22 to 0.94 mg kg^{-1} – once per month
iv. PCB level is from 0.94 to 1.88 mg kg^{-1} – six times per year
v. PCB level greater than 1.88 mg kg^{-1} – consumption not recommended

Following the recommendations it can be concluded that fish inhabit the Pechora River and studied tributaries can be consumed with no limit.

Since fish are able to metabolize and excrete PAHs rapidly,[19] only limited accumulation of these compounds was observed in the tissues of fish from the Pechora River and its tributaries. As a consequence, tissue levels of parent PAHs usually provide only limited assessment of the exposure level.[20] However, PAHs analysis also showed relatively high concentrations of several compounds of water soluble fraction of crude oil in the liver tissues of whitefish from the lower reach of the Pechora River. The data probably indicate that source of this hydrocarbon compounds are located directly at the Pechora downstream (Korovinskaya Bay).

The results of our investigation revealed different patterns of PAHs, OCCs and PCBs accumulation in whitefish, vendace and ide. These differences can be affected by variations in fat content, behavior, age, size, habitat, feeding and sexual conditions between studied fish species. Our findings confirm the results of previous studies where species specific differences in the levels of POP accumulation were investigated.[14,21, 22]

The current work also showed a great difference of POP accumulation between the liver and muscles of fish. As a rule, the liver accumulates such compounds more actively which is a logical consequence of its function of detoxicating the incoming hydrocarbons and lipophilicity of studied substances. Observed tissue differences in studied compounds accumulation was also described by Miranda et al., [23] Monosson et al., [24] and Menone et al.[25]

Conclusions

The research has proved that the assessment of the degree of hydrocarbon products, OCCs, PCBs, and PAHs impact on fish is quite complicated task. The difficulties of evaluating the effect of the substances are due to the following factors: firstly, the high degree of their metabolism within the organism; second, no standards have been developed for most substances belonging to the group. Thus PCB is

a group of substances with over 200 theoretically possible chlorinated biphenyls.[26]

Furthermore, compounds within the group may differ markedly in toxicity, so the standard set with view to an individual substance may not be relevant for the whole group. Relying on the following indicators we can state that fish in the Pechora is exposed to the effect of hydrocarbons and their derivatives: presence of heptachlor in fish muscles, relatively high total PAHs content in some coregonids (compared to other fish species).

Following international parameters, OCCs, PCBs and PAHs concentrations found in the fish could be classed as posing no risk to the fish. In river systems, however, accumulation of some organic contaminants in fish differs from that in lentic waters. Thus DDT concentration in the muscles of barbel from a lake was 0. 166 mg kg^{-1}, from a river – some 8 times less (0.021 mg kg^{-1}).[10] Hence, the conclusion about the safety of OCCs and PAHs does not reflect the actual situation. The situation requires that the changes are diagnosed by studying the processes going on at the biochemical level, first of all in the protein and lipid metabolism. There is a chance that metabolism processes in the Pechora fish now involve anthropogenic hydrocarbons. Some of the substances are extrinsic to the living nature, and the consequences of their introduction in the organism life may be unpredictable.

Acknowledgments

"ConocoPhillips" (Houston, USA) is acknowledged for financial support and "Typhoon" center for supporting analyses.

References

[1] Lukin A.A.; Dauvalter V.A.; Novoselov A.P. *The Pechora River Ecosystem in modern conditions*, Apatity, 2000. [in Russian]

[2] Wartena, E.; Evenset A. *Effects of the Komi oil spill 1994 in the Nenets Okrug, North-West Russia. Oil components and other contaminants in sediments and fish from the Pechora River,* Report No. APN 514.789.1; Akvaplan-NIVA: Tromsø; 1997.

[3] Skotvold, T.; Wartena, E.M.M; Rognerud, S. *Heavy metals and persistent organic pollutants in sediment and fish from lakes in Northern and Arctic regions of Norway,* Report No. APN 514.660.1, SFT-Report 688/97; Akvaplan-NIVA: Tromsø; 1997.

[4] Kozlovskaya, V.I.; German, A.V. Polychlorinated biphenils and polyaromatic hydrocarbons in the ecosystem of the Rybinskoye reservoir. Water Resour. **1997**, *24*, 520–527.

[5] Knutzen, J. *PAH in the aquatic environment in Norway.* Report O-87189/E-88445 NIVA, Oslo, Norway, 1989.

[6] Anderson, J.W.; Neff, J.M.; Cox, B.A.; Tatem, H.E.; Hightower, G.M. The effects of oil on estuarine animals: Toxicity, uptake and depuration, respiration. In *Pollution and physiology of marine organisms*; Vernberg, F.J., Vernberg, W., Eds.; Academic Press, Inc: New York, 1974; 285–310.

[7] Reshetyuk, A.L.; Talakina, E.I.; En'yakova, P.A. Toxicological evaluation of acenaphthene and acenaphthylene. Gig. Tr. Prof. Zabol. **1970**, *14*, 46–47. [in Russian]

[8] Rotenberg, I.S.; Mashbits, F.D. Toxicological aspects of acenaphthylene. Gig. Tr. Prof. Zabol. **1965**, *9*, 53–54.

[9] Winters, K.; O'Donnell, R.; Batterton, J.C.; Van Baalen, C. Water soluable components of four fuel oils: chemical characterization and effects in growth of microalgae. Mar. Biol. **1976**, *36*, 269–276.

[10] Rovinskii, F.Ya.; Voronova, L.D.; Afanasyev, M.I.; Denisova, A.V.; Pushkar', I.G. *Background monitoring of terrestrial ecosystem pollution with organochlorine compounds*, Hydrometeoizdat: Leningrad, 1990. [in Russian]

[11] Bespamyatnov, G.P.; Krotov, Yu.A. *Maximum permissible concentration of chemicals in the environment*. Chemistry: Leningrad, 1985. [in Russian]

[12] Bandman, A.L.; Voitenko, G.A.; Volkova, N.V.; Dikyn, P.P.; Ivanova, V.A.; Ivin, B.A. et al. *Harmful chemical substances: Hydrocarbons. Halogenated hydrocarbons*. Chemistry: Leningrad, 1990. [in Russian]

[13] Bazzanti, M.; Chiavarini, S.; Cremisini, C.; Soldati, P. Distribution of PCB congeners in aquatic ecosystems: a case study. Environ. Inter. **1997**, *23*, 799–813.

[14] Sethajintanin, D.; Johnson, E.R.; Loper, B.R.; Anderson K.A. Bioaccumulation profiles of chemical contaminants in fish from the Lower Willamette River, Portland Harbor, Oregon. Arch. Environ. Contam. Toxicol. **2004**, *46*, 114–123.

[15] Kinney, A.; Fitzgerald, E.; Hwang, S.; Bush, B.; Tarbell, A. Human exposure to PCBs: modeling and assessment of environmental concentrations on the Akwesasne reservation. Drug Chem. Toxicol. **1997**, *20*, 313–328.

[16] Garner, C.E.; Matthews, H.B. The effect of chlorine substitution on the dermal absorption of polycholorinated biphenyls. Toxicol. Appl. Pharm. **1998**, *149*, 150–158.

[17] Anderson, H.A.; Amrein, J.F. Proposed protocol for a uniform Great Lakes sport fish consumption advisory. Great Lakes fish advisory task force protocol drafting committee. Wisconsin Department of Healthand Social Services and Wisconsin Department of Natural Resources; 1993.

[18] Pellettieri, M.B.; Hallenbeck, W.H.; Brenniman, G.R.; Cailas, M.; Clark, M. PCB intake from sport fishing along the northern Illinois shore of Lake Michigan. Bull. Environ. Contam. Toxicol. **1996**, *57*, 766–770.

[19] Meador, J.P.; Stein, J.E.; Reichert, W.L.; Varanasi U. Comparative bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms. Rev. Environ. Contam. Toxicol. **1995**, *143*, 79–165.

[20] Varanasi, U.; Stein, J.E.; Nishimoto, M. In *Metabolism of Polycyclic Aromatic Hydrocarbon in the Aquatic Environment*; Varanasi, U., Ed.: CRC Press, Inc, Boca Raton: FL, 1989; 93–150.

[21] Ashley, J.T.F.; Horwitz, R.; Steinbacher, J.C.; Ruppel, B. A comparison of congeneric PCB patterns in American eels and striped bass from the Hudson and Delaware River estuaries. Mar. Poll. Bull. **2003**, *46*, 1294–1308.

[22] Haiber, G.; Schöler, H.F. Identification of Di-o,o'-cl-, Mono-o,o'-cl- and o,o'-cl-substituted PCB congeners in Neckar River fish. Chemosphere **1994**, *28*, 1913–1919.

[23] Miranda, A.L.; Roche, H.; Randi, M.A.F.; Menezes, M.I.; Oliveira Ribeiro, C.A. Bioaccumulation of chlorinated pesticides and PCBs in the tropical freshwater fish *Hoplias malabaricus*: Histopathological, physiological, and immunological findings. Environment International, **2008**, *34*, 939–949.

[24] Monosson, E.; Ashley, J.T.F.; McElroy, A.E.; Woltering, D.; Elskus, A.A. PCB congener distributions in muscles, liver and gonad of *Fundulus heteroclitus* from the lower Hudsn Riber and Newark Bay. Chemosphere, **2003**, *52*, 777–787.

[25] Menone, M.L.; Aizpun de Moreno, J.E.; Moreno, V.J.; Lanfranchi, A.L.; Metcalfe, T.L.; Metcalfe, C.D. PCBs and organochlorine in tissues of silverside (*Odontesthes bonariensis*) from a costal lagoon in Angertina. Arch Environ Contam Toxicol, **2000**, *38*, 202–208.

[26] Toutelian, V.A.; Lashneva, N.V. *Polychlorinated biphenyls*, Moscow, 1988. [in Russian]